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Marine Park Authority



# Water Quality Guidelines for the Great Barrier Reef Marine Park.

Great Barrier Reef Marine Park Authority, Townsville.



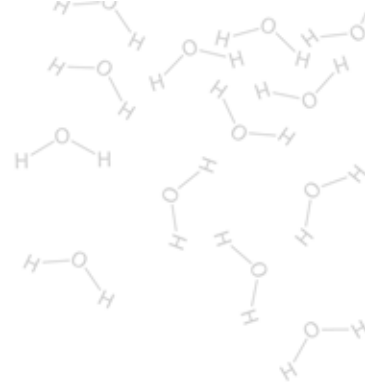
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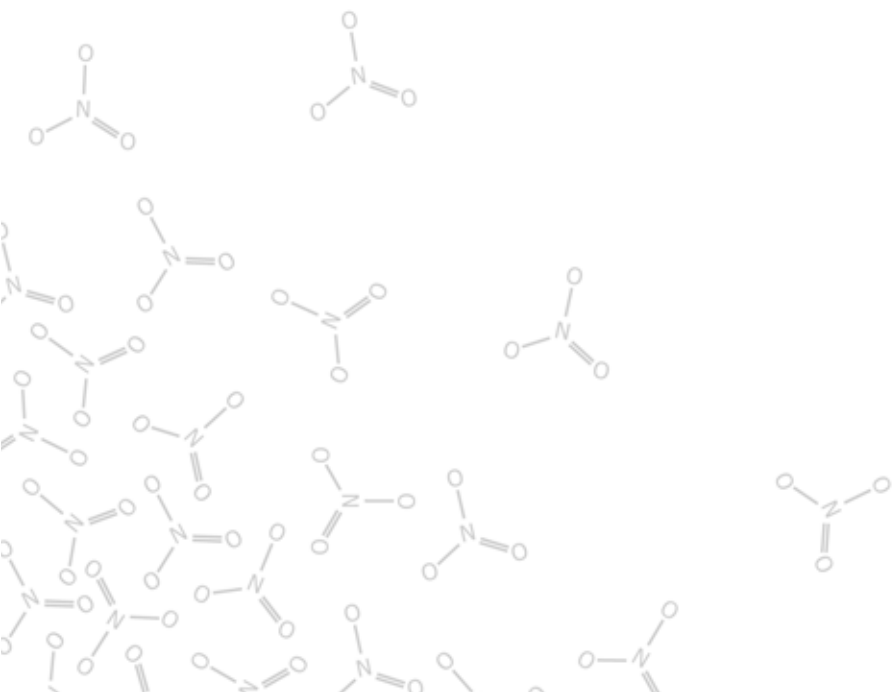
**Great Barrier Reef  
Marine Park Authority**



# **Water Quality Guidelines for the Great Barrier Reef Marine Park.**

Great Barrier Reef Marine Park Authority, Townsville.

**REVISED EDITION 2010**



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## FOREWORD

While the Great Barrier Reef is one of the richest, most complex and diverse ecosystems in the world, it is also highly vulnerable to the impacts of climate change. Adverse effects are already being observed on plants, animals and habitats in this World Heritage Area.

Good quality water is essential for the proper functioning of the Reef's ecological systems if it is to have any chance of enduring the impacts of climate change. For example, a coral's ability to recover from bleaching resulting from a rise in sea temperature is significantly reduced if it is living in degraded water.

The *Water Quality Guidelines for the Great Barrier Reef Marine Park* describe the concentrations and trigger values for sediment, nutrients and pesticides that have been established as necessary for the protection and maintenance of marine species and ecosystem health of the Great Barrier Reef.

Currently available monitoring results show that at certain times and places these trigger values are not met in the Great Barrier Reef region. Australians are responding to this challenge with farmers, graziers, communities and all levels of government working together to clean up our rivers that now carry excess fertiliser and pesticides. They are taking action to restore coastal wetlands that not only catch excess silt from floods but provide nursery habitats for many species of fish; to prevent pollution from sewage; to prevent overfishing of top predators such as sharks and to avoid the accidental loss of iconic species such as dugong and turtle.

The uptake of improved farming practices in catchments adjacent to the Great Barrier Reef is well underway with significant investment made under the Australian Government's Reef Rescue Plan. Queensland government agencies, natural resource management bodies, industries, individual land holders, research agencies, non-government organisations and the community are all working together to tackle the issues of water-borne contaminants.

Water quality research and monitoring in streams, estuaries and marine habitats will continue and the guidelines will be revised as we learn more about the complex tropical ecosystems in the Great Barrier Reef region and their responses to different environmental conditions.

I look forward to working with all of you to safeguard the future health of the Great Barrier Reef, and I thank the contributors and reviewers who have generously given their time to the development of this publication.

A handwritten signature in black ink, appearing to read 'Reichelt', with a stylized, cursive script.

Russell Reichelt  
Chair  
Great Barrier Reef Marine Park Authority

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# 1 Introduction

## 1.1 The Great Barrier Reef setting

The Great Barrier Reef is the largest reef system in the world and extends for over 2300 km along the northern Queensland (Australian) continental shelf (Figure 1). It consists of an archipelagic complex of over 2900 reefs and covers an area of approximately 344 000 km<sup>2</sup>.

The Great Barrier Reef was declared a World Heritage Area in 1981, and internationally recognised by the World Heritage Committee for its Outstanding Universal Value. It remains one of only a small number nominated for all four natural criteria under the World Heritage Operational Guidelines:

- Exceptional natural beauty and aesthetic importance
- Significant geomorphic or physiographic features
- Significant ecological and biological processes
- Significant natural habitats for biological diversity.

The Great Barrier Reef's diversity reflects the maturity of the ecosystem, which has evolved over hundreds of thousands of years. It is the world's most extensive coral reef system and is one of the world's richest areas in terms of faunal diversity. A majority of its reefs are situated on the mid- and outer-continental shelf, and are located 40 to 150 km from the mainland. A significant number of reefs (ca 750) also exist at 'inshore' or 'nearshore' sites, within 40 km of the Queensland coast (Furnas and Brodie 1996). The reefs range in size from less than one hectare to more than 100 000 hectares, and in shape from flat platform reefs to elongated ribbon reefs.

The Great Barrier Reef World Heritage Area contains more than coral reefs. The diverse range of habitats includes extensive areas of seagrass, mangrove, soft bottom communities and island communities. There are an estimated 1500 species of fish and more than 300 species of hard corals. More than 4000 mollusc species and over 400 species of sponges have been identified. The islands and cays support several hundred bird species, many of which have breeding colonies on the Great Barrier Reef.

There are currently more than 70 Traditional Owner groups with cultural connections to sea country along the Great Barrier Reef Marine Park coast. Their traditional and cultural relationship centres on story-telling, ceremonies, fishing, collecting and trading activities.

Great Barrier Reef industries such as tourism, recreational and commercial fishing are highly dependent on the marine environment. These valuable reef-based activities rely on a healthy reef ecosystem.

The Australian and Queensland governments, working with scientists, stakeholders and the community, have initiated a number of key plans and strategies aimed at halting and reversing the decline in the quality of waters entering the Great Barrier Reef. Key initiatives include:

- The Australian Government's Reef Rescue Plan, targeting improved farm management practices and supporting water quality monitoring programs
- The Australian and Queensland Government's *Reef Water Quality Protection Plan 2003* (Reef Plan)
- The Australian Government's *Coastal Catchments Initiative* (CCI)
- The Australian Government's *National Water Quality Management Strategy* (NWQMS)

- The Queensland Wetlands Program
- The Queensland Environmental Protection (Water) Policy 1997.

These guidelines were developed to support those initiatives, and in particular, to compile the currently available scientific information to provide environmentally-based values for water quality contaminants that, if reached, will trigger management actions.

These guidelines define trigger values that will be used to:

- Support setting targets for water quality leaving catchments
- Prompt management actions where trigger levels are exceeded
- Encourage strategies to minimise release of contaminants
- Identify further research into impacts of contaminants in the Marine Park
- Assess cumulative impacts on the Great Barrier Reef ecosystems at local and regional levels
- Provide an information source for Natural Resource Management bodies, industry, government and communities.

It is important to note that the levels of contaminants identified in these guidelines are not targets. Instead they are guideline trigger values that, if exceeded, identify the need for management responses.

Many management responses have already been determined through some of the programs identified above including Water Quality Improvement Plans being developed for the Great Barrier Reef catchments, regional natural resource management plans, and in industry best practice codes and management systems.

The Great Barrier Reef Marine Park Authority has worked, and will continue to work, with stakeholders and the community on what the trigger levels are, and how and where they apply.

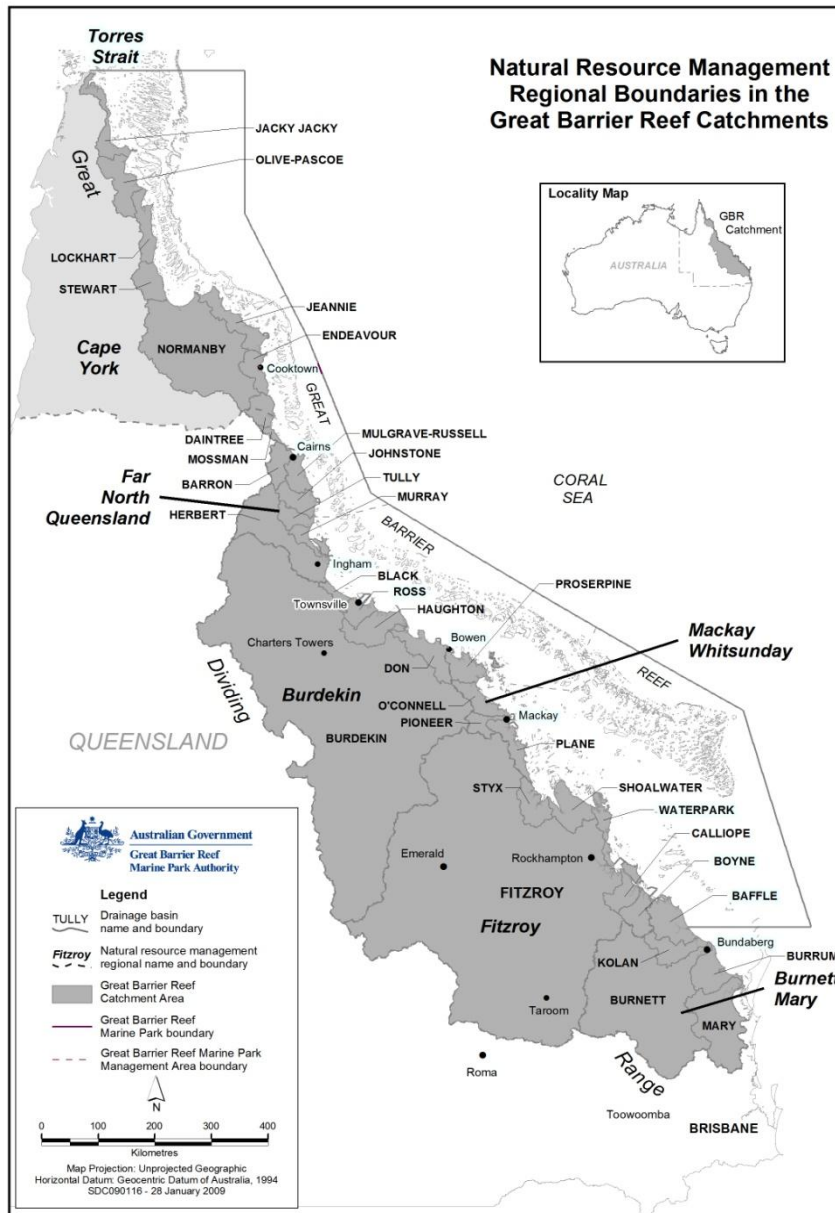


Figure 1: The Great Barrier Reef region and its catchments

## 1.2 The Australian National Water Quality Management Strategy

The Australian Government, in cooperation with state and territory governments, recognised that the development of a consistent national approach to water quality management was critical. This framework was developed and is presented in the National Water Quality Management Strategy (NWQMS) and includes the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000* (ANZECC and ARMCANZ (2000)).

The ANZECC and ARMCANZ (2000) guidelines are designed to help users assess the quality of the water resource and its ability to sustain the environmental values identified. Should the measured water quality not meet the water quality guidelines, the waters may not be able to

maintain the environmental values. Management action should be triggered to either more accurately determine whether the water really is fit for purpose or to rectify the problem.

The ANZECC and ARMCANZ (2000) guidelines were not intended to be applied as mandatory standards. They recognised that there is significant uncertainty associated with the derivation and application of water quality guidelines across the many and varied waterways in Australia and New Zealand. Rather, the water quality guidelines should be viewed as being a trigger for further management action.

ANZECC and ARMCANZ (2000) emphasises the need to develop and adapt the guidelines to suit the local area or region. ANZECC and ARMCANZ (2000) incorporate protocols and detailed advice to assist users in tailoring the water quality guidelines to local conditions. A referential approach to deriving guidelines for coastal waters of the Great Barrier Reef is difficult as much of these waters are already affected by polluted waters from the mainland. In particular, the guidelines recognise that for the long-term management of any water resource, there must be:

- A designated and clearly articulated set of environmental values
- An understanding of the connections between human activity and environmental quality
- Unambiguous goals for management
- Appropriate water quality objectives
- Effective management frameworks, including cooperative, regulatory, and adaptive management strategies.

The broad national management strategy for application at a regional/local level is as follows (Figure 2):

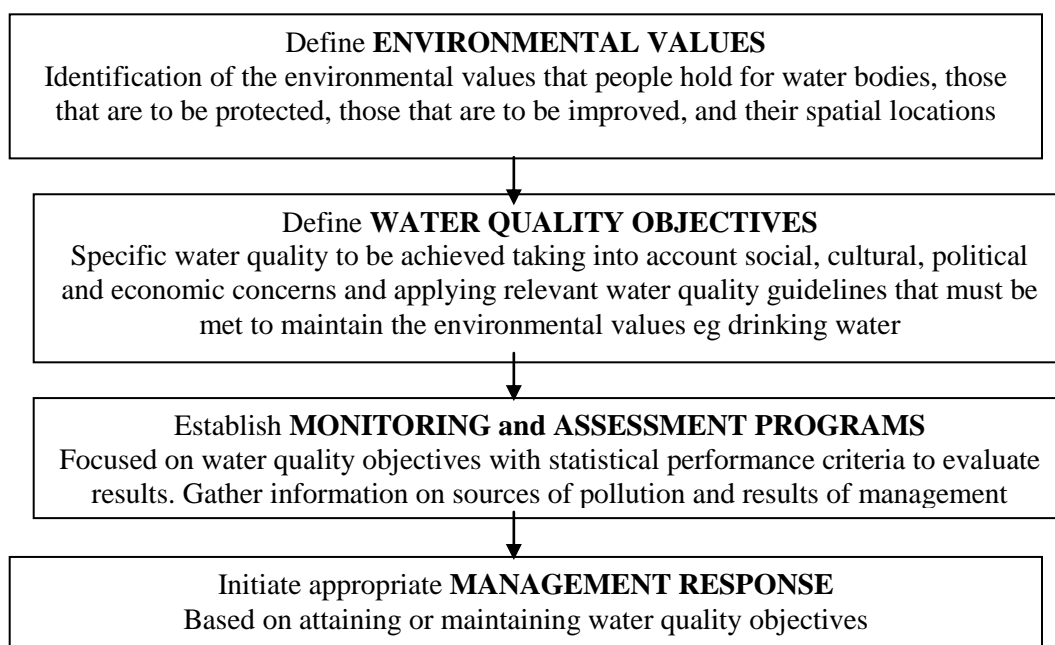


Figure 2: Management framework for applying the ANZECC and ARMCANZ (2000) guidelines

The Water Quality Guidelines for the Great Barrier Reef Marine Park have been developed to address the first two steps of the ANZECC and ARMCANZ (2000) process described in Figure 2. It is the intention that steps 3 – 4 will be addressed through the Marine Monitoring Program, and

through Water Quality Improvement Plans being developed for the Great Barrier Reef catchments and in regional natural resource management plans.

### ***1.3 Environmental values of the Great Barrier Reef World Heritage Area***

Environmental values are particular values or uses that a water body fulfills, or it is desired that it fulfill, in its communal use as a resource. There are currently six environmental values described in the ANZECC and ARMCANZ (2000) guidelines:

- Aquatic ecosystems
- Primary industries (irrigation and general water uses, stock drinking water, aquaculture and human consumption of aquatic foods)
- Recreation and aesthetics (primary recreation, secondary recreation, visual appreciation)
- Drinking water
- Industrial water
- Cultural and spiritual values.

All water resources will have at least one of these environmental values. The Great Barrier Reef is both a World Heritage Area and a multiple use Marine Park. As set out in section 1.1 above, the values of the Great Barrier Reef include aquatic ecosystems, primary industries, recreation and aesthetics, and cultural and spiritual values. Many vessels and resorts rely on desalination for drinking water, and there is an increasing interest in desalination as a source of fresh water for adjacent coastal communities.

These guidelines have addressed the values of the Great Barrier Reef taking into account local and regional scale ecological and use values. Where two or more agreed environmental values are defined for a water resource, a more conservative set of guidelines will prevail. For the Marine Park the more conservative guideline will usually arise from the aquatic ecosystem protection value.

The management intent for waters with aquatic ecosystem values depends on their current aquatic ecosystem condition and community needs and aspirations. Four levels of aquatic ecosystem condition and management intent are recognised in the Australian National Water Quality Management Strategy, two of which are currently considered relevant for Great Barrier Reef waters.

The two levels of condition are high ecological value, and slightly disturbed. The management intent for waters with high ecological value aquatic ecosystems is to maintain the natural values of the ecosystems, including biotic, physical form, riparian vegetation, flow and physicochemical water quality attributes. For slightly disturbed aquatic ecosystems the management intent is to maintain their current values, and improve their slightly disturbed attributes back towards their natural values.

Influence areas of river discharges from the Great Barrier Reef catchments (Maughan et al 2008) have been assigned an aquatic ecosystem condition of slightly to moderately disturbed. However, within these slightly to moderately disturbed waters, some areas have been explicitly recognised for their high ecological value. For example, the Marine National Park and Preservation Zones (GBRMPA 2003) are in place to protect representative examples of the entire range of habitats and biological communities (bioregions) that are found in the Great Barrier Reef. These zones are assigned a high ecological value even where they fall within the river discharge influence area.

Information will continue to be collected on water quality and aquatic ecosystem health through a number of monitoring programs to inform us about the waters that need improvement. An adaptive management approach will allow the findings of the monitoring to feedback to any necessary management actions.

All areas outside of the river discharge reaches are assigned an aquatic ecosystem value, as well as a high ecological value condition. In recognition of the relatively undeveloped Cape York Natural Resource Management catchments all Marine Park waters adjacent to these catchments are assigned a high ecological value.

## **2 Primary management considerations**

### **2.1 Environmental concerns**

Protection of the ecological systems of the Great Barrier Reef World Heritage Area from water-borne contaminants is recognised as one of the critical issues for management of the World Heritage Area (Haynes et al 2001, 2006). Evidence derived from modelling and sampling indicate that the export of sediments and nutrients from southern disturbed catchments to the marine environment has risen dramatically over the last 150 years (Furnas 2003).

There is also increasing evidence concerning the contamination of coastal ecosystems with a range of modern pesticide residues (Haynes et al 2000a, Mitchell et al 2005, Shaw and Müller 2005). Degradation of inshore reefs of the Great Barrier Reef has been associated with increased terrestrial run-off of contaminants in the region between Port Douglas and the Whitsunday's (Udy et al 1999, van Woesik et al 1999, Fabricius and De'ath 2004; Fabricius et al 2005). Damage to both inshore and outer-shelf reefs of the central Great Barrier Reef from crown-of-thorns starfish (*Acanthaster planci*) outbreaks has been attributed to increased terrestrial nutrient runoff (Brodie et al 2005). Degraded reefs in the regions, contrast starkly with unimpacted reefs offshore of Cape York (Fabricius et al 2005).

The potential impacts of declining water quality on ecosystems in the Great Barrier Reef lagoon have been synthesized and reviewed in recent years (Hutchings and Haynes 2000, Haynes et al 2001, Williams 2001, Baker 2003, Furnas 2003, Brodie et al 2005, Fabricius 2005, Fabricius et al 2005, Schaffelke et al 2005, Brodie et al 2008). The 2005 *Special Edition of the Marine Pollution Bulletin* (Volume 51) provides a benchmark of information on a broad range of water quality issues for the Great Barrier Reef (Hutchings and Haynes 2005).

There is an immediate need to improve current land management regimes to minimise diffuse runoff and its impact on the Great Barrier Reef (Brodie et al 2001, Brodie and Mitchell 2005, Brodie et al 2008).

### **2.2 Management goals and policies**

The Australian and Queensland governments have established programs aimed at halting and reversing the decline in the quality of water entering the Great Barrier Reef. The current programs operate over the ten years from 2003 to 2013.

The quality of the water entering the Reef is determined by a number of factors, primarily: the level and types of contaminants entering rivers and streams; the capacity of areas in the catchment to filter the water (such as riparian areas and wetlands), and the mitigation of downstream impacts of other actions such as land clearing, intensification of agriculture and degradation of wetlands, which can result in increased sediment or chemicals flowing into the river system.

The Australian Government's Reef Rescue Plan seeks to deliver significant reductions in the discharge of contaminants to the Great Barrier Reef by, amongst other things, improving on-farm management practices.

Water Quality Improvement Plans developed by natural resource management bodies, or local government, in collaboration with government, industry and communities are an important component of the strategy for managing water resources. These plans are prepared consistent with the Framework for Marine and Estuarine Water Quality Protection. The key features include:

- The environmental values of the coastal water

- The water quality issues (eg contaminant levels and sources) and subsequent water quality objectives
- The load reductions of contaminant/s to be achieved to attain and maintain the water quality objectives
- Extension and adoption of management actions to address issues
- Industry codes of practice and farm management systems.

This document derives evidence based guideline trigger values expected to sustain the health of the marine ecosystems. At this time its focus is on land-sourced contaminants. For parameters that are not presented in the guidelines they default back to the Queensland Water Quality Guidelines 2006, which in turn defaults to the National guidelines.

We know that under present conditions concentrations sometimes exceed those set in these guidelines (particularly in flood events). Many actions are already being undertaken to improve water quality and as those that reduce contamination of catchment waters are widely implemented the situation is expected to improve. Careful consideration will be made of any monitoring results that are over the trigger values in deciding if any action is needed. The Great Barrier Reef Marine Park Authority acknowledge and emphasise the importance of working with people to set appropriate short-term and long-term targets for the catchments that they live in, and supporting activities in their area that will improve local water quality and subsequently protect the health of the Great Barrier Reef.

For pesticides, non-naturally occurring contaminants, the preferred concentration for the health of the marine ecosystem is actually zero as even at very low concentrations effects can still occur, albeit not necessarily lethal. However the Guidelines apply widely accepted scientific rigour to the derivation of its trigger values in this first publication of the Great Barrier Reef guidelines and hence the concentrations presented within the document. Some natural resource management groups who have completed their Water Quality Improvement Plan development have adopted objectives of zero detectable pesticide concentrations for ambient marine water quality with the support of the community and have our support for this more conservative response (eg Mackay Whitsunday Natural Resource Management Group 2008).

### **2.3     *Variability and uncertainties***

There are still many uncertainties about the effects that are, or may be, caused by contaminants in waterways, as well as the generation and delivery of them.

#### Effects

Biological effects levels for the pesticides and biocides in these guidelines are based on measurements under laboratory conditions. The need to translate these laboratory-based results to expected real world responses means that the assessment factors for conversion from acute to chronic, and the pathway to the ecosystem at risk each have uncertainties associated with them. There is also a lack of tropical marine species testing.

Measurable endpoints of sediment and nutrient biological effects are not as clear as the pesticide and biocide effects. Cape York water quality has been used as a reference to represent historic natural condition and mixed statistically with data on effects levels and monitored values from the Great Barrier Reef waters (De'ath and Fabricius 2008). Trigger levels resulting from this approach might be more conservative, but it is apparent that the levels derived this way closely agree with the real data from areas of the Great Barrier Reef with higher species richness and lower per cent cover of macro algae. Furthermore, setting the trigger values conservatively is appropriate given the World Heritage status of the Great Barrier Reef.



Additive, synergistic and antagonistic effects complicate the setting of guideline trigger values, but are still poorly understood. Many of the contaminants discussed in these guidelines are delivered in flood events that occur in the summer. Warm, fresh, sediment laden, nutrient rich, chemical cocktail waters arrive on the ecosystems at a time when they may already be under pressure from high air temperatures as well as sensitive reproductive phases of their life cycles. Future findings may determine that, in consideration of this mixture being delivered, guideline trigger values for individual components may need to be revised downward.

#### Generation

During the past two decades the export of sediment and nutrients from Great Barrier Reef catchments has been estimated using a range of modelling techniques. Models applied to Reef catchments include SedNet, Annex, EMSS, E2, LISEM, and Savanna. Of these approaches, the one that has been applied most frequently and received the most attention, both from the modelling community, as well as the policy/decision making community is SedNet. It utilises spatially-distributed data to calculate a mean annual mass balance for an entire catchment as well as each river link within a drainage network. As with all models SedNet is based on a set of assumptions and the model is only as good as the data that goes into it. Acknowledged uncertainties exist in particular around the following areas:

- Lack of a mechanism to account for storages of sediment in the catchment
- The need for improved understanding of hydrological process and hence, sediment and nutrient transport
- The need for speciation of nutrients (rather than modelling just total nitrogen and total phosphorus)
- A finer spatial and temporal resolution of landscape processes needs to be understood and modelled
- The landscape being generally poorly characterised, and input data for the models needs to be improved (eg hydrology, rainfall, soils, Digital Elevation Models)
- Knowledge of how to scale up and down processes, parameters and data is relatively weak
- The need to explicitly recognise and routinely report uncertainty in the model, and place confidence limits on all model predictions.

Effort is being made to address these matters and improvements in particular catchments have seen models rerun with improved data (eg Tully Murray, Fitzroy). Better modelling gives us greater confidence of the key sources and fates of particular contaminants and will help to target the management actions that might need to be taken to address water quality issues.

Many management practices that are expected to minimise losses off farms have not had their water quality improvement effectiveness quantifiably determined. Work is being done to provide quantification which will help in making decisions about the most effective changes.

## **2.4 Review**

New information is always arising. The Great Barrier Reef Marine Park Authority plans to update and improve these guidelines over time as more information becomes available and as understanding improves on the effect of different qualities of water on ecosystem health.

A joint project between the Great Barrier Reef Marine Park Authority, James Cook University and the Australian Institute of Marine Science is underway to improve the understanding of the susceptibility of tropical marine species to pesticides as well as the combined effects of elevated sea surface temperatures (SST) and pesticides on tropical organisms. Understanding the

interactive effects of pesticides and climate change on seagrasses and corals is considered to be important for the future management of the Great Barrier Reef Marine Park.

A number of projects are underway that have been designed to improve the understanding of system responses. Some of the key projects are:

- Ongoing trials and demonstration farms applying practices to validate the expectations that they will improve the quality of water leaving farms, and minimise losses of contaminants.
- Catchment model validations using monitored data to adjust factors and make them run more realistically.
- Tracing materials from the upper catchment to the Reef to better understand the source of sediments.
- Marine and estuarine indicators and thresholds of concern for ecosystem health.

One of the primary providers of science to support decision-making is the Marine and Tropical Sciences Research Facility. Annual Research Plans are prepared that provide much more detail on investigations underway in the scientific community that focus on many of these matters and can be viewed on the worldwide web ([www.rrrc.org.au/publications/arp.html](http://www.rrrc.org.au/publications/arp.html)).

### **3 Spatial considerations**

#### **3.1 *Boundaries along the Great Barrier Reef***

The Burnett-Mary, Fitzroy, Mackay-Whitsundays, Burdekin Dry Tropics, Wet Tropics, and Cape York natural resource management bodies working with governments have the responsibility to set targets for water bodies in their regions. Latitudinal differences in effects levels of the parameters presented in these guidelines were not evident in the data. However, current condition is markedly different in the respective regions. Analyses of the current condition of sediment and nutrients were run separately for each of the marine water bodies adjacent to the six natural resource management regions that border the Great Barrier Reef. The current condition of water bodies is outside the primary purpose of these guidelines but the mean annual values and standard errors for these parameters are contained in a separate report (De'ath and Fabricius 2008) published by the Great Barrier Reef Marine Park Authority and provide an indication of the scope of water quality improvement needed for sediment and nutrient parameters.

#### **3.2 *Boundaries across the shelf***

Five distinct water bodies have been defined for these guidelines:

- Enclosed coastal
- Open coastal
- Midshelf
- Offshore
- The Coral Sea

The approximate distances of the water body delineations for each of the natural resource management regions is discussed in the following paragraphs and is presented in Table 1.

The enclosed coastal water body is adopted from the Queensland Water Quality Guidelines 2006 (EPA 2006). This adoption facilitates complementarity between Queensland and Australian Government water quality guidelines in the Great Barrier Reef Marine Park.

The seaward limit of the enclosed coastal water body is the cut-off between shallow, enclosed waters near the estuary mouth and deeper, more oceanic waters further out. For estuaries that flow directly into open oceanic waters the seaward limit is defined as the mouth of the estuary enclosed by adapting the semicircle bay rule (6.1, Article 7, *Maritime Limits and Baselines 1978*). The semicircle rule adapted is:

*“A passage or estuary is closed by a semi-circle, with its diameter at the natural entrance(s) to the passage or estuary, drawn to extend beyond the entrance(s)”.*

Generally, the entrance is defined by the downstream limits of the drainage catchment of the estuary (the heads). Where the heads are undefined, the catchment limits will need to be estimated using other landscape elements.

Within an enclosed bay or strait, the seaward limit may be much further out from the mouth, depending on local hydrological and topographic conditions.

For estuaries flowing into an enclosed bay or strait, the seaward limit of the enclosed coastal water body should ideally be determined by site-specific studies to determine where the effective limit of freshwater mixing extends. Such studies should take into account factors such as bathymetry, water quality, salinity, residence times of water, aerial or satellite imagery, and seagrass distributions.

If no additional information is available, the default seaward limit should be based on the six metre depth contour below lowest astronomical tide.

The enclosed coastal water body has been comprehensively mapped for some areas (eg Fitzroy) and a program is underway to complete the remaining areas. Until the water body is mapped the open coastal guideline trigger value will be applied landward from its edge to the semicircle at the mouth of most river openings to the ocean.

The open coastal, midshelf and offshore water body delineations adopt a slightly modified version of the De'ath and Fabricius (2008) relative distance across the shelf boundaries, to recognise the enclosed coastal water body described above (Table 1). The De'ath and Fabricius (2008) relative distance delineation assumes the shoreline has a value of zero, and the edge of the continental shelf has a value of one.

The De'ath and Fabricius (2008) coastal water body delineation extends from 0 – 0.1; inshore water body from 0.1 – 0.4; and offshore water body from 0.4 – 1.0 (Figure 3; Table 1). The modification adopted in these guidelines is that the landward edge of the coastal water body delineation commences at the seaward boundary of the enclosed coastal water body rather than the shoreline. In addition, the coastal water body is renamed open coastal and the inshore water body is renamed midshelf.

Table 1: Approximate water body delineations of the open coastal, midshelf and offshore marine water bodies in the six NRM regions

| NRM region        | Open Coastal (km)   | Midshelf (km) | Offshore (km) |
|-------------------|---------------------|---------------|---------------|
| Burnett-Mary      | EC <sup>*</sup> -7  | 7-28          | 28-270        |
| Fitzroy           | EC <sup>*</sup> -20 | 20-80         | 80-340        |
| Mackay-Whitsunday | EC <sup>*</sup> -15 | 15-60         | 60-280        |
| Burdekin          | EC <sup>*</sup> -12 | 12-48         | 48-180        |
| Wet Tropics       | EC <sup>*</sup> -6  | 6-24          | 24-170        |
| Cape York         | EC <sup>*</sup> -6  | 6-24          | 24-250        |

EC The seaward edge of the enclosed coastal water body as described above.

In the enclosed coastal and open coastal water bodies, re-suspension of sediments and associated contaminants occurs in the prevailing south-east wind regime at wind speeds greater than 25 knots (Orpin et al 1999). This area is also regularly subjected to freshwater plumes from major Great Barrier Reef catchment rivers (Devlin et al 2001). In some areas tidal re-suspension also contributes strongly to the enclosed coastal turbid zone (Kleypas 1996). Turbidity is generated by winds along the coast. These effects are not evident in the offshore water body, although in more extreme flood events can affect the midshelf water body.

Coral Sea waters are contained within the Marine Park, seaward of the edge of the continental shelf. At this time trigger values have not been determined for this water body and no further reference will be made to it.

The delineation into enclosed coastal, open coastal, midshelf and offshore water bodies is particularly relevant for comparison of the current status of identified water bodies against guideline trigger values.

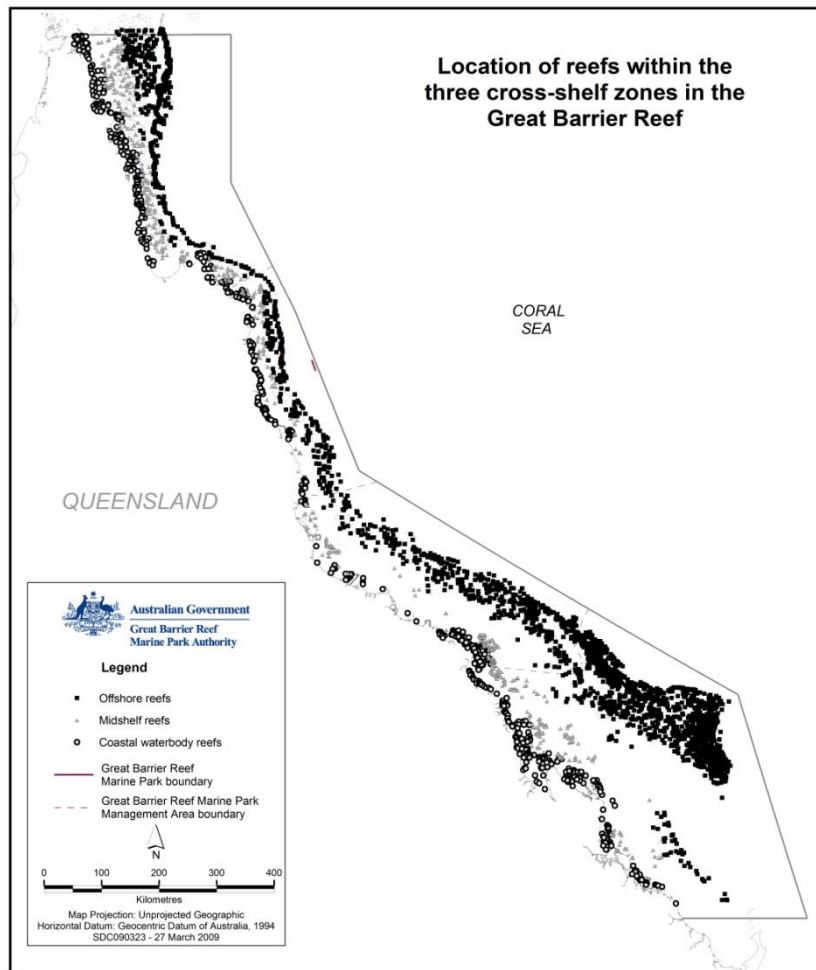


Figure 3: Location of reefs within the three cross-shelf water bodies in the Great Barrier Reef

## 4 Temporal considerations

### 4.1 *Acute versus long-term exposure*

The concentrations of chlorophyll and some of the nutrients vary by more than an order of magnitude over time, depending on wind, tides, weather and season. Few experimental data are available to assess causal relationships between long-term exposure (months to years) and contaminants and biotic responses (De'ath and Fabricius 2008). In some cases, short-term exposure to high contaminant loads has the same outcome as prolonged exposure to lower values (Weber et al 2006). Figure 4 shows the conceptual relationship between loads and durations of exposure to sediments, turbidity, salinity and benthic irradiance, with indicative effects concentrations set for relatively robust coral species. These values would require downward correction for more sensitive species.

In the enclosed coastal water body these guidelines adopt the concentrations for the various physico-chemical parameters directly from the Queensland Water Quality Guidelines 2006 (EPA 2006). These guidelines are generally for application in normal base-flow conditions. Under extreme high or low-flow conditions, guideline application requires careful consideration. Further discussion on this consideration is presented in section 4 of the Queensland Water Quality Guideline 2006 (EPA 2006).

For slightly-to-moderately disturbed waters the guideline values are compared with the median of values at a test site (section 4 of EPA 2006). For high ecological value waters the guideline values are compared with the 20<sup>th</sup>, 50<sup>th</sup> and 80<sup>th</sup> percentile of the natural values in these waters. The latter being presented only where adequate baseline data is available.

For open coastal, midshelf and offshore water bodies De'ath and Fabricius (2008) argue that short periods of high nutrient concentrations are ecologically significant, and such values are not reflected in median values. In contrast to medians, mean annual values capture and reflect (at least partially) both the frequency and magnitude of 'water quality events' (eg floods and other events that result in high values), and annual average values are therefore used as the measure for trigger values.

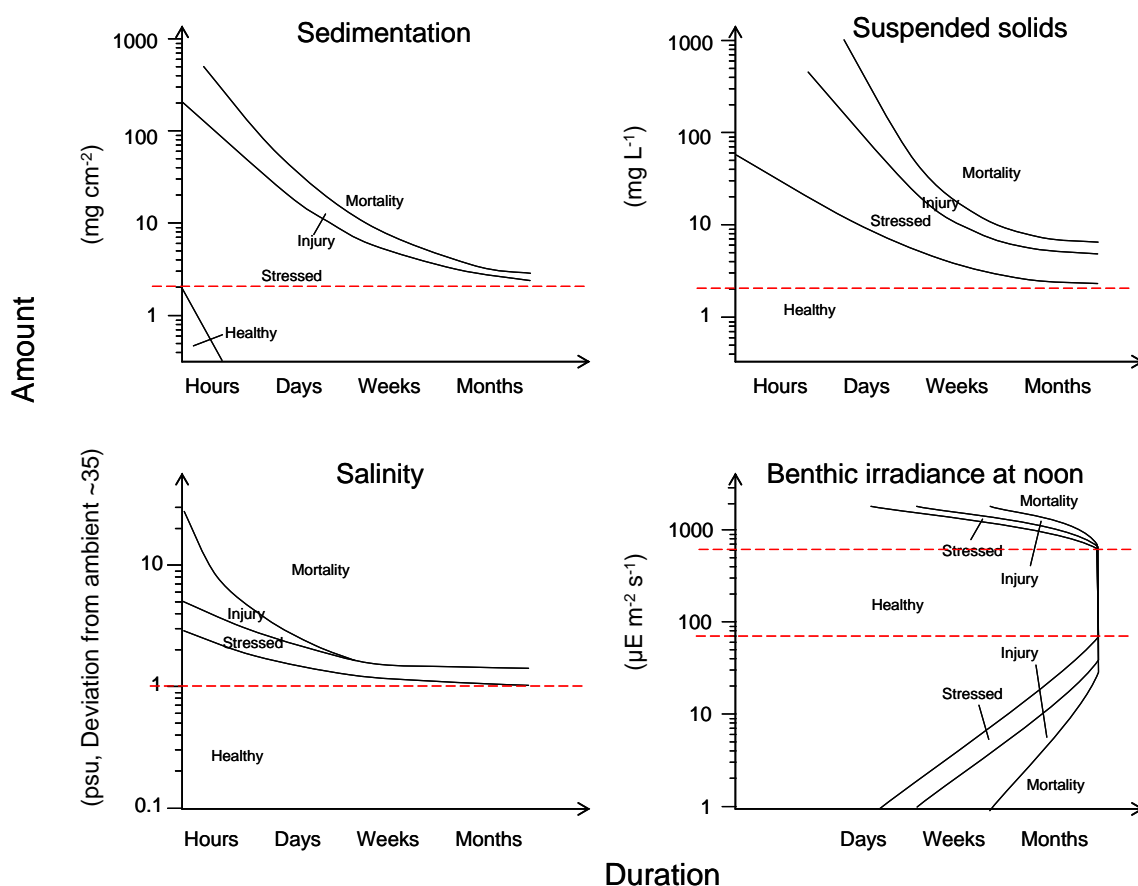


Figure 4: Conceptual relationships (De'ath G and Fabricius K (2008))

The curves are conceptual and exposure values are only indicative, and apply to relatively robust inshore corals. More sensitive species will respond at lower loads and/or shorter durations. Salinity is scaled as the deviation from the mean marine salinity (35 psu). The effects of variation in salinity are not well known, but as low-salinity events are usually limited from days to weeks, it is assumed that salinity concentrations are more important than the duration of exposure, resulting in an intersection of the injury and mortality curves. Like salinity, benthic irradiance is a stressor both at low and high levels. In general, corals have wide tolerance ranges to benthic irradiance, and only very low levels for prolonged periods of time, and very high levels result in stress. The tolerance of low benthic irradiance varies with the ability of corals to compensate through heterotrophic nutrition.

## 4.2 Seasonal changes in water quality

Concentrations of chlorophyll and some of the nutrients vary seasonally, related to higher nutrient inputs, temperatures and benthic irradiance in summer than in winter (Furnas 2003). Long-term averages of chlorophyll are about 70 per cent higher in March than in September in the Great

Barrier Reef (Figure 5, De'ath 2007b, Brodie et al 2007). River floods carrying new nutrients and sediments into the Great Barrier Reef are also most commonly observed in the late wet season when monsoonal rainfall is greatest (Devlin et al 2001, Furnas 2003, Brodie et al 2003). The relative contribution of river floods versus other intrinsic and extrinsic factors to this long-term seasonal pattern is not well understood. At intra-annual time scales, other processes add variability to nutrient and suspended solid concentration. Probably most importantly, concentrations in the inshore area are strongly dependent on wind and wave driven resuspension of material from the seafloor, and blooms of the nitrogen-fixing *Trichodesmium* sp. can also significantly increase nutrient concentrations.

Although trigger values should ideally include additional separate trigger values for flood conditions, this is currently impractical due to the unpredictable timing and varying intensity of monsoonal floods. Seasonally adjusted long-term averages rather than flood values are therefore used to define guideline trigger values for the time being, and are presented where sufficient data was available. Summer values are defined as January to March: winter values as July to September.

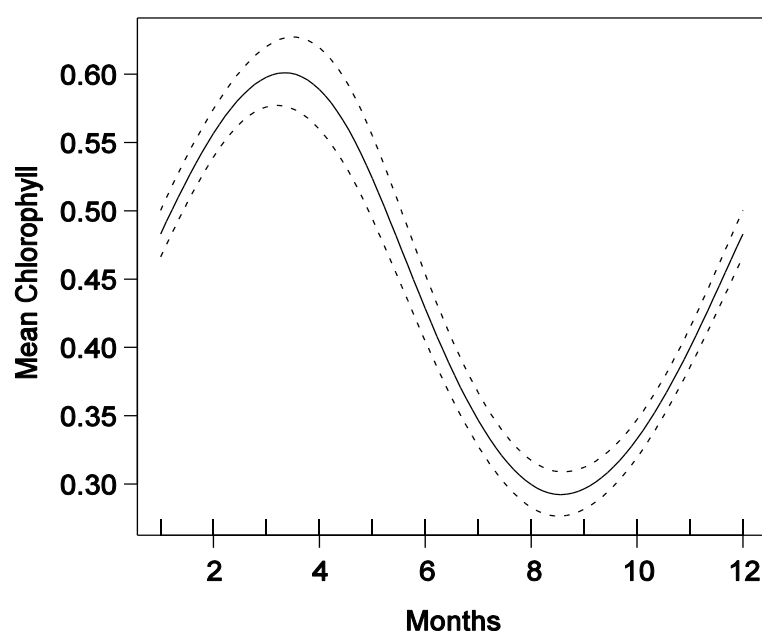


Figure 5: Estimated seasonal variation of chlorophyll concentrations in the Great Barrier Reef, averaged over all locations of the Great Barrier Reef (from De'ath 2007b)

## **5 Determination of appropriate guideline trigger values**

### **5.1 Introduction**

A water quality guideline is a numerical concentration limit or narrative statement recommended to support and maintain a designated use of the water resource. ANZECC and ARMCANZ (2000) has developed guidelines with the intention of providing some confidence that environmental values will be maintained should they be achieved. These guidelines are a refinement intended to protect marine ecosystems of the Great Barrier Reef from exposure to particular contaminants. The derived trigger values are physical, biological and chemical specific estimates designed to initiate further management action should they be exceeded.

Exceedance of a trigger value indicates that there is a potential for an impact to occur, but does not provide certainty that an impact will occur. Exceedance activates management action. Action may include whether the source has been contained, evaluating whether any impact on ecosystem health has occurred, changing a land management practice, or any number of alternatives.

These guidelines have focused on deriving guideline trigger values for common rural diffuse land-borne contaminants. Justification for this focus comes from the Reef Plan supporting science that rural diffuse sources contribute the majority of contaminant loads to the Great Barrier Reef lagoon. For parameters that are not presented in these guidelines the default is to apply the Queensland Water Quality Guidelines 2006, which in turn default to the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000*.

### **5.2 Indicator types**

The types of organisms that were considered for these guidelines came from the following taxonomic groups:

- Fish
- Crustaceans
- Molluscs
- Annelids
- Echinoderms
- Green Algae
- Red Algae
- Macrophytes
- Corals

### **5.3 Derivation of sediment and nutrient guideline trigger values**

The enclosed coastal water body trigger values have been adopted directly from the Queensland Water Quality Guidelines 2006 (EPA 2006). Reflecting current data availability, this version provides regional guidelines for the Central Coast and Wet Tropics, as well as sub-regional guidelines for the Daintree high ecological value waters. No regional guideline is available for the Eastern Cape at this time. Regional guideline values were derived from the 80th percentiles of data collected at three or more reference sites.

Enclosed coastal water body slightly-to-moderately disturbed waters guideline values are the median of values at a test site (section 4, EPA 2006). High ecological value waters guideline values are the 20<sup>th</sup>, 50<sup>th</sup> and 80<sup>th</sup> percentiles of the natural values in these waters. The latter being presented only where adequate baseline data is available.

For open coastal, midshelf and offshore water bodies the Australian Institute of Marine Science (AIMS) was commissioned to analyse the more than ten years of sediment and nutrient data that



have been collected from the Great Barrier Reef and derive the trigger values for relevant parameters to protect the health of the marine ecosystem.

Nine water quality parameters were analysed: Secchi depth, chlorophyll, suspended solids, particulate, dissolved and total nitrogen, and particulate, dissolved and total phosphorus (De'ath and Fabricius 2008).

Two independent approaches were combined to define guideline trigger values for water quality:

- Modelled relationships between the condition of reef biota, and the parameter. Secchi depth and water column chlorophyll concentration were used to identify the highest mean annual chlorophyll and lowest Secchi values that prevented high macroalgal cover and low coral and octocoral richness
- Analyses of the spatial distribution of water quality in Cape York waters. Since Cape York is subject to only minor modification of land use its' water quality condition was taken to be consistent with reference sites (European Community 2005, Environmental Protection Agency 2006).

The Great Barrier Reef Marine Park Authority expects that the second approach will generate substantial discussion about the appropriateness of applying Cape York water quality to other waters of the Great Barrier Reef. As was discussed in section 2.3 the Great Barrier Reef Marine Park Authority acknowledges that there are still many uncertainties about the generation and delivery of contaminants to waterways, as well as the effects that are, or may be, caused by them. At this time the Great Barrier Reef Marine Park Authority takes the opportunity to remind the reader that the proposed application of these guidelines considers this uncertainty (section 2.3 and 2.4). It is a much broader question (and outside the primary purpose of these guidelines) to consider what target might be achievable, given the current state of the system and the current level of technology.

Furthermore, the following considerations are relevant when deciding on guideline trigger values of stressors based on laboratory experiments:

- **Susceptibility varies greatly between species**, and depends on size and life history stage within species. For example, whole-colony mortality from sedimentation is more likely in small than in large colonies, while temperature stress may be size independent. Tolerance of low benthic irradiance may also be independent of colony size, while the settlement behaviour of coral larvae is very responsive to changes in benthic irradiance/turbidity. As ecosystem sensitivity depends on the most sensitive species or processes/functions, guideline trigger values should be set to protect the most sensitive species, life history forms or ecosystem functions.
- **Toxicity of mixtures** such as additive, synergistic and antagonistic effects complicates the setting of guideline trigger values, but is still poorly understood. For example, crustose coralline algae are far more sensitive to damage by sedimentation when traces of the herbicide diuron are present (Harrington et al 2005). Other examples are that the uptake of dissolved inorganic nutrients in some benthic macro algae is diffusion limited (Hurd 2000), and that benthic macro algae may use additional nutrients predominantly where benthic irradiance is not limiting. Similarly, climate change is expected to increase the frequency of disturbances to reefs (through bleaching, ocean acidification, and the intensity of drought – flood cycles and cyclones; Fabricius et al 2007a), hence the importance of good water quality is even more important to maximise resilience and facilitate reef recovery.
- **Both concentration and duration of exposure often co-determine the severity of a response**. Prolonged or chronic exposure to low levels of contaminants can be as detrimental as short acute exposure to high levels of contaminants. For example, the effects of sedimentation and high temperature increases linearly with amount and duration of exposure ie a coral exposed to high levels of sedimentation for a short period

of time shows a similar level of photophysiological stress compared to one that is exposed to low levels of sedimentation for a prolonged period of time. Guideline trigger values should provide protection against both chronic and acute effects.

- **Exposure-response curves of biota tend to be non-linear**, and in some cases both upper and lower guideline trigger values may be required. For example, corals are highly tolerant of exposure to a wide range of nutrient and light levels, and only very low and very high levels lead to disease and mortality. In contrast, sedimentation invokes a monotonic response, with coral health declining with increasing exposure to sedimentation. Corals can also grow in a wide range of turbidity, with very low particle densities resulting in reduced heterotrophic nutrition, and very high density leading to reduced photosynthetic carbon gain. However, corals undergo photo adaptation in response to fluctuating light availability by adjusting zooxanthellae densities, which results in stress from photo inhibition for several days after particles have settled out, and stress from low photosynthetic carbon gains for several days after the water has become more turbid (Anthony and Hoegh-Guldberg 2003). Photo adaptation takes around 7 – 10 days, during which the coral photophysiology does not perform at optimum rates. Therefore it is the variability in turbidity rather than the absolute value that determines the level of stress at all but extreme levels of turbidity.
- **Exposure to nutrients, turbidity and sediments varies naturally along spatial gradients.** For example:
  - Light loss from turbidity will have far greater effects on coral communities in deep water than in shallow water.
  - Rates of sedimentation are generally greater in sheltered reef embayments and on lower back reef slopes than on wave-exposed reef slopes. Poorly flushed sheltered, deeper reef slopes in which stressors remain for extended periods are therefore more susceptible to impacts than well-flushed shallow areas from which stressors dissipate more rapidly.
- **Toxicity and mortality thresholds based on short-term exposure experiments are not adequate endpoints to define trigger values**, as long-term exposure at sublethal stress levels can still result in ecosystem degradation, due to reduced growth, reproduction and recruitment, and higher rates of mortality. Measures of ecosystem health that integrate over long periods of time (macro algal cover, reduced species richness in corals and octocorals) were therefore chosen. High macro algal cover is widely accepted as an indicator of reef degradation, and is also a causative agent of both mortality and failed reproduction in corals and a range of other reef organisms. Reduced species richness is generally the outcome of selective mortality, slower growth or failed reproduction of the more sensitive species exposed to severe environmental conditions.

These complicating factors are not specific to coral reefs but typical for many ecosystems and support the methods chosen for deriving guideline trigger values.

The guideline trigger value for Secchi depth is a mean annual water clarity minimum for each water body. However, areas with high tidal ranges experience intense resuspension regimes while chlorophyll and many of the nutrient concentrations in this zone are low. It is therefore advisable to decrease the guideline value for water clarity for areas with greater than 5 m tidal ranges, and an arbitrary value of 20 per cent is suggested for this purpose (eg Broad Sound). In the longer term, local tides and wave height might be included as additional factors in the models to assess ecosystem responses.

Trigger values for the other sediment and nutrient parameters derived with these methods are presented as annual mean concentrations that should not be exceeded. Mean values were chosen since exposure to high concentrations was considered ecologically important and De'ath and Fabricius (2008) argue that percentiles (eg medians) do not adequately reflect acute high values.

To account for seasonal variability, regional means were also calculated for the summer and winter quarters (wet and dry season, respectively) for each cross-shelf position within each of the natural resource management regions. Current conditions of waters adjacent to each natural resource management area are collated in De'ath and Fabricius (2008).

#### **5.4 Toxicity data for deriving pesticide guideline trigger values**

The preferred method for the derivation of toxicant trigger values is to collect data from multi-species toxicity testing ie field or mesocosm test that are able to represent the complex interactions of all species within an ecosystem (ANZECC and ARMCANZ 2000). However, many of these tests have not been conducted largely due to the significant costs associated with undertaking these studies and the difficulty in ascribing causality to specific stressors whilst removing confounding agents.

Biological effects concentrations data established by direct toxicity testing are presented in tables in this document.

Guideline trigger values for pesticides were derived as outlined below. Chronic exposure was defined for multi-celled organisms as being greater than 96 hours, and for single-celled organisms as being equal to or greater than 72 hours (Warne 2001).

- *High reliability guideline trigger values –*

A high reliability trigger value requires chronic no observed effect concentration (NOEC) toxicity data for five different species that belong to at least four different taxonomic groups to apply the BurrliOZ statistical distribution method (Warne 2001). Chlorpyrifos was the only pesticide that met this requirement. These guidelines adopt the high reliability trigger value from the ANZECC and ARMCANZ (2000) guidelines for chlorpyrifos.

- *Moderate reliability guideline trigger values –*

Where the minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups was met, the BurrliOZ statistical distribution method (Campbell et al 2000) was used to derive guideline trigger values for ecosystem protection.

Effects concentrations for particular endpoints were entered into the BurrliOZ statistical distribution software (Campbell et al 2000) to determine concentrations protective of 99, 95 and 90 per cent of species.

Where a no observable effects concentration (NOEC) was available for a species this was used in preference to applying assessment factors to either chronic or acute lethal concentration or effects concentration to fifty per cent of the test species (LC or EC50s) toxicity measures (Warne 2001). Lowest observable effects concentrations (LOECs) were not used in the derivation of trigger values.

Where an acute to chronic ratio was available it was applied as an assessment factor to convert acute LC or EC50s to chronic NOECs before entering the data into the software. Where there is no acute to chronic assessment factor, the default assessment factor of 10 was applied. A factor of 5 was applied to convert chronic EC or IC50s to chronic NOECs.

Where two toxicity values were reported for the same endpoint in the same species the geometric mean of the two results was entered (Van de Plassche et al 1995).

- *Low reliability guideline trigger values* – Where the minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups is not met a low reliability guideline can be derived in a number of ways. Except for MEMC and hexazinone these guidelines adopt the ANZECC and ARMCANZ (2000) method of using a freshwater guideline with lower reliability.

There was sufficient EC50 or LC50 data available for hexazinone to apply the division of the lowest of the acute values by 100 (OECD 1992) to provide a low reliability guideline trigger value.

ANZECC and ARMCANZ (2000) did not include an assessment of MEMC. Data have since become available on the toxicity of this fungicide. Since there are data on only one taxonomic group an assessment factor of 1000 was applied to the effect concentration to convert an acute effect to a chronic for the guideline trigger value.

## 5.5 *Level of protection*

The goal of the Great Barrier Reef Marine Park Authority is the long-term protection and maintenance of the Great Barrier Reef Marine Park and World Heritage Area. In considering the establishment of trigger values, for pesticides (and the one biocide derived) concentrations protective of 99, 95 and 90 per cent of species have been calculated.

For high ecological value water bodies, a guideline concentration that is protective of 99 per cent of species is ideal. In section 1.3, the environmental values of the Great Barrier Reef Marine Park were discussed. Regardless of the current condition of the waters (high ecological value, slightly-to-moderately-disturbed or highly-disturbed), aquatic ecosystem protection is the highest environmental value currently applied to the entire World Heritage Area.

The trigger values are chosen to be applied in the Great Barrier Reef Marine Park case regardless of the current condition of the ecosystems, or indeed regardless of the flow of water. Even in ecologically highly-disturbed trawl grounds reaching effect levels of pesticides and biocides on the species being trawled would be unacceptable. Therefore, trigger values for these parameters as derived in these guidelines apply to all of the five water bodies at the derived concentration protective of 99 per cent of species. Our aim will be that for any water in the marine park, the concentrations are below the guideline trigger values although it is acknowledged that, for some of the time, for some of the waterways, they are currently likely to be exceeded during seasonal events.

Notwithstanding the application to all water bodies, where the assessment of current condition is better than the long-term guideline trigger values presented here, or the state or national guidelines, the precautionary long-term approach is to adopt an objective that is equal to current condition so that water quality does not degrade (eg in some cases in the Mackay Whitsunday Water Quality Improvement Plan 2008, Rohde et al 2006; 2008). The Great Barrier Reef Marine Park Authority wholeheartedly support the implementation of more stringent objectives, and the implementation of strategies to achieve them. These guidelines are based on scientific evidence of effect levels in accordance with the national strategy.

In order to ensure the health of the marine ecosystem significant consideration must be given to the preservation of food webs, in particular the primary producers. Given the mode of action of many of the pesticides it is possible that a higher weighting should be given to effect responses that occur in plants rather than in animals. At present, no weighting is applied in the statistical distribution application and so the data will tend to be biased towards the more acute mortality endpoints on animals such as fish and crustaceans that require extrapolation to chronic effects.

There is also a lack of data relating to the toxicity of many contaminants to those primary producers in the tropical marine ecosystem.

Finally, additive, synergistic and antagonistic effects complicate the setting of guideline trigger values, and are still poorly understood. Further research on additive, synergistic and antagonistic effects of various contaminants, their interactions with each other and the influence of additional stressors on the observed toxicity (eg whole effluent toxicity) is currently underway and will inform future revisions of this document.

## **5.6      *Consideration of sublethal effects***

In the last four to five years, there has been quite a lot of research published on photosynthesis, gross primary production and carbon uptake suppression effects of a number of pesticides. These responses are generally reversible, and are not universally accepted as appropriate endpoints for deriving toxicity guidelines. They have been left out of derivations in these guidelines.

However, there is concern that these responses may be an indicator of sublethal impacts, the minimisation of which could prove critical to the health and protection of the ecosystem. The concern about sublethal effects is heightened particularly if additional environmental stressors are involved, eg high temperatures (section 6.3), storm damage, sedimentation, elevated nutrient levels etc. The consequence of inclusion of this sublethal data in derivation of trigger values for particular pesticides is presented in section 6.6 primarily for future consideration, completeness and a precautionary awareness.

Species such as the coral *P. damicornis* that are dependent on photosynthesis for energy contributions are more sensitive to the effects of pesticides in terms of reproductive development and may be bioindicators of ecosystem impacts. Further research on these responses is recommended.

## **6 Guideline trigger values**

### **6.1 Introduction**

Each water quality guideline trigger value is discussed in the relevant section below. Information used in the determination of the water quality trigger value for sediment and nutrients is extracted from De'ath and Fabricius (2008).

Guideline trigger values have been derived for the following physical and chemical parameters:

- Water clarity (Secchi depth)
- Chlorophyll a (as a proxy for dissolved inorganic nitrogen)
- Suspended solids
- Particulate nitrogen
- Particulate phosphorus
- Sedimentation
- Temperature
- Several pesticides and one biocide.

### **6.2 Sediments and nutrients**

The enclosed coastal water body guideline trigger values are adopted from the Queensland Water Quality Guidelines 2006 (EPA 2006). This adoption facilitates a complementarity between Queensland and Australian Government water quality guidelines in the Great Barrier Reef Marine Park.

For open coastal, midshelf and offshore water bodies a large number of studies and reviews exist that have demonstrated that high levels of nutrient and sediment lead to deteriorating ecosystem health in coral reefs (reviewed in Fabricius 2005) and many other benthic systems. Some of the studies that quantified exposure levels and physiological and ecological effects on coral reef biota are listed and summarised in De'ath and Fabricius 2008. This data supports the choice of the derivation approach for sediment and nutrient parameters outlined below.

The review shows that most experiments were not designed to determine trigger or target values, because:

- Most of the studies do not follow internationally accepted ecotoxicity protocols
- Most studies that investigate acute short-term exposure to high concentrations do not usually determine lethal or half-way effects concentrations (LC50 or EC50)
- Few studies investigate the effects of chronic exposure, and in most of these, the 'no observed effects concentrations' (NOEC) are not systematically determined
- Response data are generally available for one or few species of corals, but rarely for any other trophic level (eg algae, crustacean or fish species).

The determination of the guideline trigger values therefore applied the approaches outlined in section 5.3.

Delineation into open coastal, midshelf and offshore water bodies is relevant for comparisons of current condition of identified water bodies against the guideline trigger values. Since these comparisons are not the focus of these guidelines they have not been included. However, the comparisons have been collated (De'ath and Fabricius 2008) and will be important background material for informing what catchment actions might need to be taken to deliver reductions in the inputs to the Great Barrier Reef waters, and how that might be achieved.

### 6.2.1 Water clarity (Secchi depth) and chlorophyll *a*

Lack of water clarity is a key indicator of poor water quality and is an essential environmental factor for phototrophic organisms that dominate coral reefs, seagrass meadows and the seafloor microphytobenthos (De'ath and Fabricius 2008).

Since inorganic nutrients are quickly taken up by phytoplankton, the effects of increased nutrient loads may be expressed as increased phytoplankton biomass, which is readily measured as chlorophyll *a* concentration, a biological trophic status indicator of the water body (Brodie and Furnas 1994). There are extensive data sets for chlorophyll *a* concentrations in waters of the Great Barrier Reef. Data summaries and analyses have been published eg Brodie and Furnas 1996, Furnas and Brodie 1996, Brodie et al 1997, Furnas and Mitchell 1997, Devlin et al 2001, Haynes et al 2001, Furnas 2003, Brodie et al 2005.

The enclosed coastal water body guideline trigger values are adopted from the Queensland Water Quality Guidelines 2006 (EPA 2006). Regional guideline values are derived from the 80th percentiles of three or more reference sites. Sub-regional guidelines are available for Daintree waters and can be referenced in the Queensland Water Quality Guidelines 2006 (EPA 2006).

For the remaining water bodies a different methodology was applied to derive the trigger values. These two water quality parameters explained 38 per cent of the variation in phototrophic coral richness, 29 per cent for macroalgal cover, and 25 and 21 per cent of richness in hard coral cover, respectively (De'ath and Fabricius 2008). Due to their important roles, the availability of extensive data, and their inclusion in ongoing monitoring programs through semi-automated monitoring stations, most analytical effort was given to water clarity (here measured as Secchi disk depth, in m) and total chlorophyll ( $\mu\text{g/L}$ ). The highest chlorophyll and Secchi values that prevented high macroalgal cover and prevented major reductions in coral and octocoral richness were identified. These values are in the range of 0.4-0.5  $\mu\text{g/L}$  mean annual chlorophyll and 10-15 m Secchi depth (Figure 6).

The following water quality data sets were used (more details of the data and methods are described in De'ath, 2007):

- Water clarity based on Secchi depth (m): a composite of Department of Primary Industries and Fisheries seagrass monitoring data (Rob Coles) and Australian Institute of Marine Science data (Miles Furnas and co-workers, K. Fabricius and co-workers).
- Total chlorophyll ( $\mu\text{g/L}$ ): A data set composed of the data from the Great Barrier Reef Marine Park Authority and Australian Institute of Marine Science long-term chlorophyll monitoring program over the period 1992-2006, and the Australian Institute of Marine Science lagoon water quality chlorophyll data.
- Lagoon water quality data: Collected by Miles Furnas and co-workers (AIMS) between 1988 and 2006. These include a suite of physical and chemical water quality data, including chlorophyll (chl ( $\mu\text{g/L}$ )), suspended solids (SS (  $\text{mg/L}$ )), particulate phosphorus (PP) and particulate nitrogen (PN) ), total dissolved phosphorus and nitrogen (TDP and TDN) and total phosphorus (TP = PP + TDP) and total nitrogen (TN = PN + TDN).

Another important nutrient-related interaction on reefs of the Great Barrier Reef, and through the Indo-Pacific generally, is that between the coral-eating crown-of-thorns starfish (*Acanthaster planci*) and reef condition. It is now believed that outbreaks of *A. planci* are associated with broad scale nutrient enrichment from land run-off and subsequent phytoplankton blooms leading to enhanced survivorship of *A. planci* larvae (Brodie et al 2005). The critical chlorophyll *a* concentration range at which larval survivorship becomes significantly enhanced is 0.5 – 0.8  $\mu\text{g/L}$  (Brodie et al 2005). This is further support for the guideline trigger value for chlorophyll *a* concentration to be in the order of 0.5  $\mu\text{g/L}$  in the larval period of *A. planci* (November to February) to ensure *A. planci* outbreaks are minimised.

Based on the two approaches outlined in section 5.3, and the supporting evidence of the COTS survivorship threshold, guideline trigger values were derived for mean annual water clarity (Secchi depth) and mean annual chlorophyll concentration for the open coastal and midshelf water bodies. Where data for the offshore water body demonstrated better water quality than derived trigger values the current condition of those water bodies is adopted as the guideline value.

Areas with high tidal ranges experience intense resuspension regimes while chlorophyll and many of the nutrient concentrations in this zone are low. It is therefore advisable to decrease the guideline value for water clarity for areas with greater than 5 m tidal ranges (eg Broad Sound) and an arbitrary value of 20 per cent is suggested for this purpose. In the longer term, local tides and wave height might be included as additional factors in the models to assess ecosystem responses.

It is important to emphasise that although improvements in water quality to below the suggested trigger levels will lead to substantial ecosystem benefits, the trigger levels represent an achievable compromise between the current water quality status and that of a pristine system.

Table 2: Guideline trigger values for water clarity and chlorophyll *a*

| <b>Parameter\Water Body</b>  | <b>Enclosed coastal<br/>(Wet Tropics/Central Coast)</b> | <b>Open<br/>coastal</b> | <b>Midshelf</b> | <b>Offshore</b> |
|--|---|-------------------------|-----------------|-----------------|
| <b>Secchi (m)<br/>(minimum mean annual<br/>water clarity) <sup>1</sup></b> | 1.0/1.5   | 10                      | 10              | 17              |
| <b>Chl <i>a</i> (µg/L) <sup>2</sup></b>                                    | 2.0   | 0.45                    | 0.45            | 0.4             |

<sup>1</sup> At shallower depths Secchi will be visible on the seafloor. Guideline trigger values for water clarity need to be decreased by 20% for areas with greater than 5 m tidal ranges. Seasonal adjustments for Secchi depths are presently not possible due to the lack of data.

<sup>2</sup> Chlorophyll values are ~40% higher in summer and ~30% lower in winter than mean annual values.



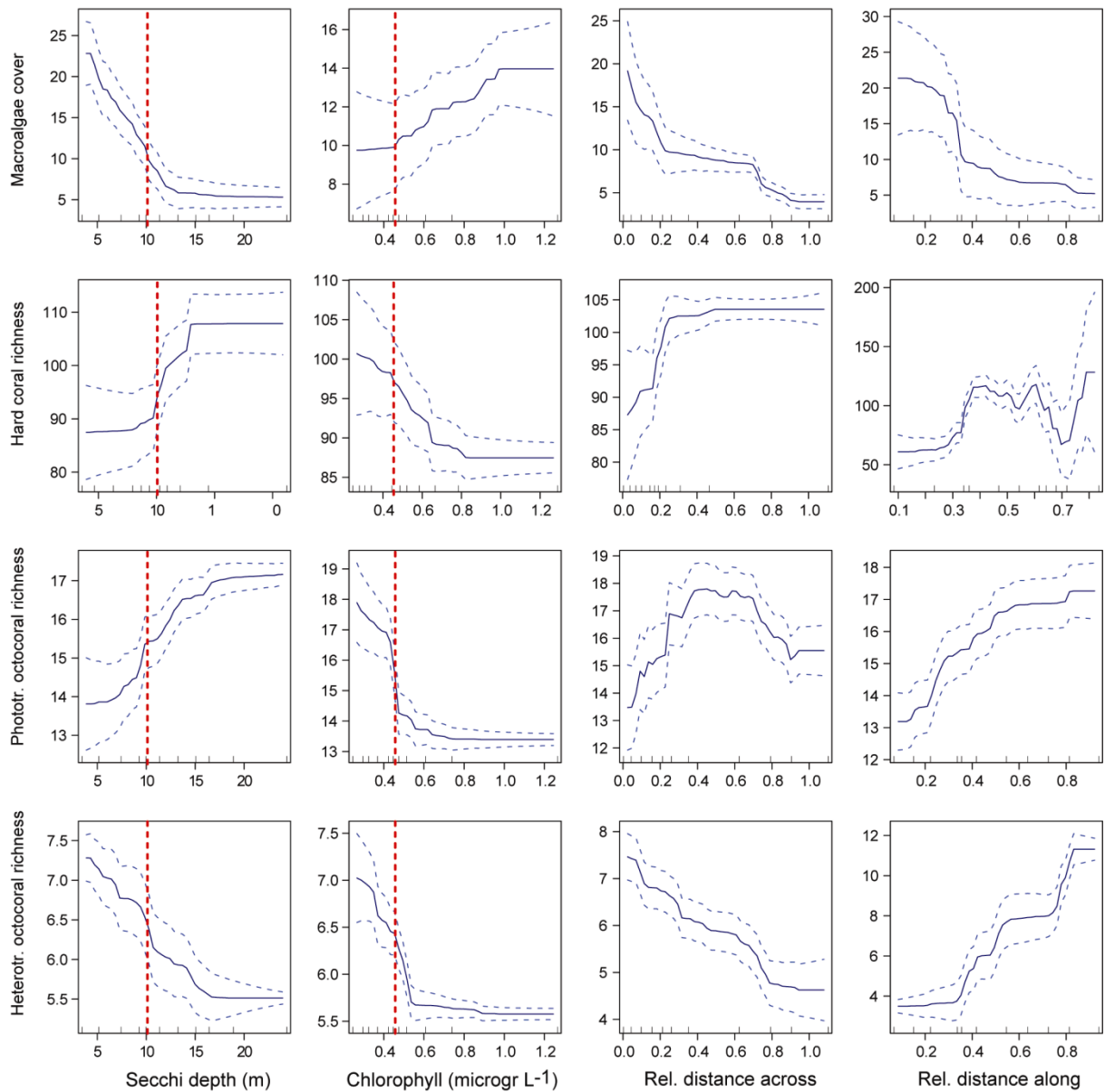


Figure 6: Partial effects of Secchi and chlorophyll concentration on ecosystem status

The vertical dashed line indicates values found in coastal waters of Cape York. Relative distance across and along were included in the model but not shown here. The plots suggest substantial improvement in reef status (higher biodiversity of hard corals and phototrophic octocorals, lower macroalgal cover) at water clarity of 5 - 15 m Secchi depth and chlorophyll of 0.3 – 0.6  $\mu\text{g/L}$ .

### 6.2.2 Suspended solids, particulate nitrogen and particulate phosphorus

Due to the high correlation between particulate nitrogen, particulate phosphorus, suspended solids and Secchi, it is not possible to resolve their individual effects on ecosystem health (although it is clear that they do have effects) and inclusion of all variables simultaneously leads to spurious conclusions about those effects (De'ath and Fabricius 2008).

To obtain approximate guideline trigger values, to provide some measure of quantum of improvement required in the current status of the water quality of these parameters, the responses of biota to each of the water quality variables SS, PN and PP were analysed separately, with relative distance across and along being included in all models (Figure 7). Note that in contrast to the previous analyses, the effects of these analyses are not additive. Partial effects plots for biotic responses and predictive errors for biotic responses to Secchi and chlorophyll were similar when both variables were analysed separately compared to when both were included in the model simultaneously (not shown).

Macroalgal cover increased about four-fold with SS increasing from 1.2 to 2.0 mg/L, and remained high above 2.0 mg/L. Macroalgal cover also increased by more than 50 per cent (from 7 to 11 per cent) with PN increasing from 0.9 to 1.6  $\mu\text{mol/L}$  (12.6 to 16.8  $\mu\text{g/L}$ ), and by ~40 per cent (from 8 to 11 per cent) with PP increasing from 0.04 to 0.14  $\mu\text{mol/L}$  (1.24 to 4.34  $\mu\text{g/L}$ ).

Hard coral richness steeply declined with SS, with highest values at less than 0.8 mg/L SS and low richness at greater than 2.0 mg/L. It also declined with PN and PP, with highest values at less than 1.0  $\mu\text{mol/L}$  PN (14  $\mu\text{g/L}$ ) and less than 0.06  $\mu\text{mol/L}$  PP (less than 1.86  $\mu\text{g/L}$ ) and low richness at greater than 1.8  $\mu\text{mol/L}$  PN and greater than 0.10  $\mu\text{mol/L}$  PP (25.2 and 3.1  $\mu\text{g/L}$ ).

The declines in phototrophic octocoral richness were much steeper than those of the hard corals. Richness was highest at less than 1 mg/L SS, 1.0  $\mu\text{mol/L}$  PN, and 0.05  $\mu\text{mol/L}$  PP (14 and 1.55  $\mu\text{g/L}$ ). Richness was up to 50 per cent lower when SS was greater than 2.0 mg/L SS, 1.6  $\mu\text{mol/L}$  PN and 0.10  $\mu\text{mol/L}$  PP (22.4 and 3.1  $\mu\text{g/L}$ ). Heterotrophic richness did not respond much to SS and PN, and only weakly declined with PP increasing above 0.08  $\mu\text{mol/L}$  (2.48  $\mu\text{g/L}$ ).

The mean annual values for coastal and midshelf waters in Cape York are 2.24 and 1.39 mg/L SS, respectively (De'ath and Fabricius 2008). For PN, they average 1.49 and 1.48  $\mu\text{mol/L}$  (20.86 and 20.71  $\mu\text{g/L}$ ), respectively, and for PP, these values are 0.090 and 0.080  $\mu\text{mol/L}$  (2.79 and 2.48  $\mu\text{g/L}$ ).

Based on the biotic responses and the concentrations found in Cape York, guideline trigger values of maximum annual means are selected for SS, PN and PP for the open coastal and midshelf water body. For PN and PP, these suggested similar trigger values are supported by both the concentrations found at the reference site and those obtained from the response curves. For SS, the response curves suggested that trigger values should be lower than the concentrations presently found in the coastal zone of Cape York, to prevent extensive macroalgal cover and loss of biodiversity. The offshore water body current condition shows better water quality than the derived trigger values. The Great Barrier Reef mean of all the offshore water bodies is adopted here as the guideline value.

Table 3: Guideline trigger values for SS, PN, and PP

| Parameter <sup>1</sup> \Water Body | Enclosed coastal<br>(Wet Tropics/Central Coast) | Open<br>Coastal | Midshelf | Offshore |
|------------------------------------|---|-----------------|----------|----------|
| SS (mg/L)                          | 5.0 <sup>2</sup> /15                            | 2.0             | 2.0      | 0.7      |
| PN ( $\mu\text{g/L}$ )             | -   | 20              | 20       | 17       |
| PP ( $\mu\text{g/L}$ )             | -   | 2.8             | 2.8      | 1.9      |

<sup>1</sup> Seasonal adjustments for SS, PN and PP are approximately  $\pm 20$  per cent of mean annual values.

<sup>2</sup> No regional data was available for suspended solids for the Wet Tropics. The current condition mean annual concentration for the enclosed coastal water body is adopted here as a guide.

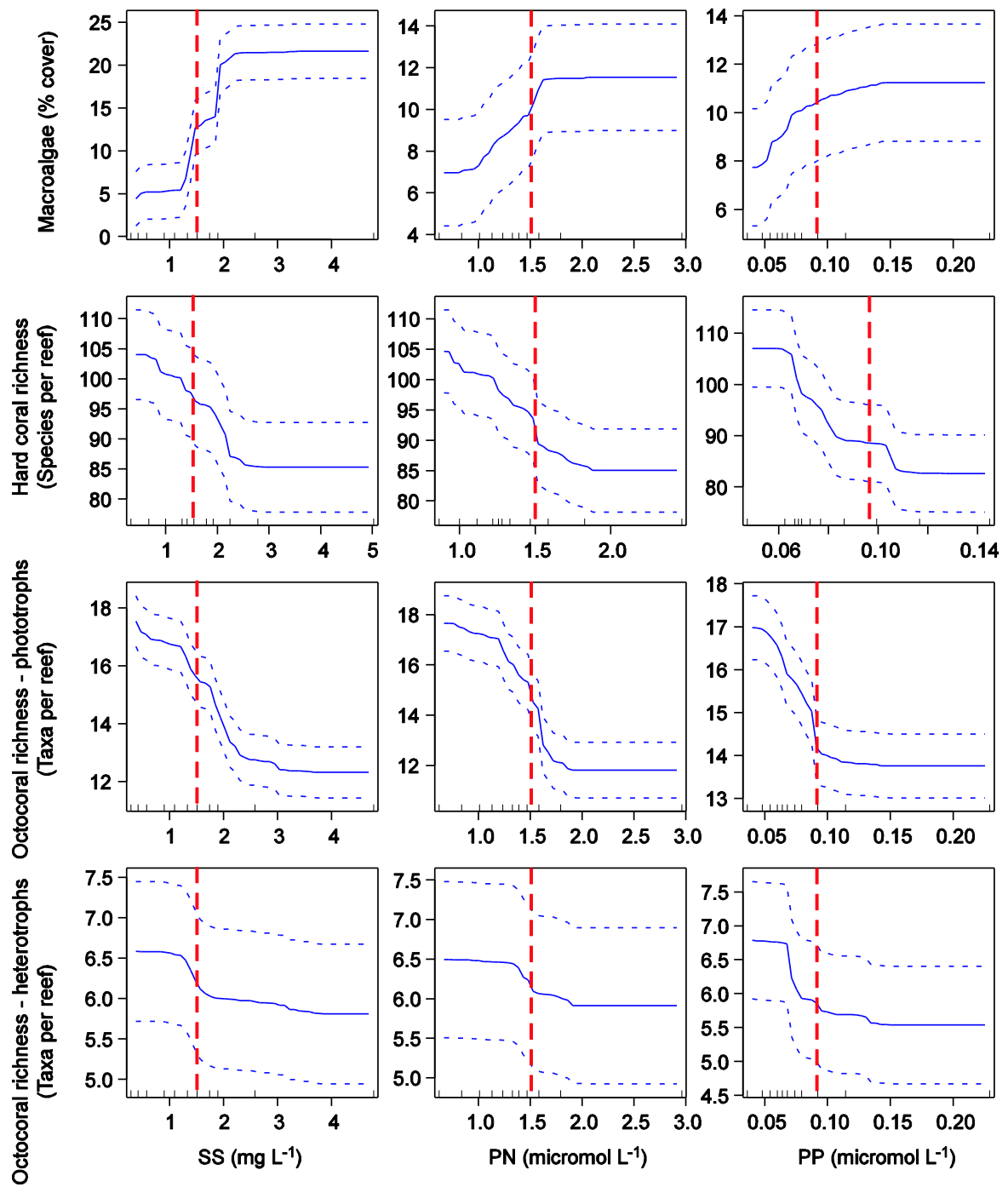


Figure 7: Partial effects of SS, PN and PP on the four measures of ecosystem health  
Dashed vertical lines show trigger levels.

### 6.2.3 Sedimentation

Fine sediments can affect corals through smothering and abrasion caused by direct settlement (Rogers 1990, van Katwijk et al 1993, Riegl 1995, West and Van Woesik 2001, McClanahan and Obura 1997, Philipp and Fabricius 2003). Corals use energy to remove sediment through polyp motion and mucus shedding, and this may reduce coral fitness (Riegl and Branch 1995).

Sediment impacts on corals can include changes to coral population structure and colony size, altered growth forms, inhibition of recruitment and reduced growth and survival (Tomascik and Sander 1987, Rogers 1990, Babcock and Davies 1991, Wittenberg and Hunte 1992, Gilmour 1999, Anthony 2000, Anthony and Fabricius 2000, Babcock and Smith 2002).

Low concentrations of sediments and particulate mucopolysaccharides released by bacteria and other microorganisms can coat corals (Fabricius and Wolanski 2000, Fabricius et al 2003). The removal of such aggregates is energy expensive, creating a metabolic drain that may reduce reproductive capacity and the organism's capacity to grow (Stafford-Smith 1993, Riegl and Branch 1995, Telesnicki and Goldberg 1995).

Recovery from sedimentation stress varies between species (Stafford-Smith and Ormond 1992, Wesseling et al 1999). Early life stage corals are at most risk from accumulated sediment through prevention of larval settlement (Hodgson 1990, Gilmour 1999), or burial of the juvenile recruit (Babcock and Davies 1991, Babcock and Mundy 1996, Fabricius et al 2003). Sedimentation is also suspected to adversely impact abundance of crustose coralline algae, and to influence the development of algal turfs. Both of these effects will compromise coral recruitment (Birrell et al 2005, Harrington et al 2005).

A number of independent experiments have shown that a chronic exposure to  $<10 \text{ mg/cm}^2/\text{day}$  sedimentation induces significant coral recruit mortality (De'ath and Fabricius 2008). Rogers (1990) proposed a threshold for healthy reefs at  $10 \text{ mg/cm}^2/\text{day}$  sedimentation, moderate to severe effects on corals at  $10$  to  $50 \text{ mg/cm}^2/\text{d}$ , and severe to catastrophic effects at  $>50 \text{ mg/cm}^2/\text{day}$ .

Other studies have shown that chronic levels of sedimentation higher than  $3 \text{ mg/cm}^2/\text{day}$  induces mortality in coral recruits, while levels higher than  $10 \text{ mg/cm}^2/\text{day}$  reduce coral species richness, coral cover, coral growth rates, calcification, net productivity of corals, and reef accretion (De'ath and Fabricius 2008).

Fabricius et al (2003) and Weber et al (2006) have shown that sedimentation effects not only increase with the amount of sediment but also with organic and nutrient content and with decreasing grain size.

Experimental evidence suggests that  $10 \text{ mg/cm}^2/\text{day}$  sedimentation is valid in areas with coarse calcareous sediments, but trigger levels need to be lower where sediments are largely of terrigenous origin, of small grain size or of high organic content (De'ath and Fabricius 2008).

Based on existing experimental and field evidence, a sedimentation trigger value of a maximum mean annual value of  $3 \text{ mg/cm}^2/\text{day}$ , and a daily maximum of  $15 \text{ mg/cm}^2/\text{day}$  (De'ath and Fabricius 2008) is set. This value is set with a low confidence, as more field data are needed. The value chosen is expected to guard against excessive coral recruit mortality and includes an uncertainty factor for higher organic content or small grain sizes.

Hydrodynamic settings determine to what extent ecosystem stress is due to sedimentation and to what extent due to turbidity. In areas of low hydrodynamic energy, stress due to sedimentation will exceed the stress due to light attenuation. At high hydrodynamic energy, where sediments tend to remain in suspension, the reverse is true (De'ath and Fabricius 2008). In the longer term, the Great Barrier Reef Marine Park Authority will consider the development of sediment quality guidelines. Such guidelines would aim to include trigger values for sediment nutrient concentrations, which at elevated levels may cause toxicity through the development of excess pore water ammonia and hydrogen sulphide.

A guideline trigger value is established at a **maximum mean annual sedimentation rate of  $3 \text{ mg/cm}^2/\text{day}$** , and a daily maximum of  $15 \text{ mg/cm}^2/\text{day}$ .

### 6.3 *Temperature*

Temperature is included in these guidelines because it is clear that corals suffer physiological stress when water temperatures increase above normal maxima. The most visible sign of this stress is coral bleaching, which can lead to coral death if elevated temperatures persist for 6-10 weeks. Sea temperature increases of 1°C above the long-term average maximum (calculated from the last 20 years) are all that is required to trigger coral bleaching (Hoegh-Guldberg 1999, Coles and Brown 2003). Both the intensity and duration of temperature anomalies are important in determining the timing and severity of bleaching responses. Higher temperatures can cause bleaching over a shorter exposure time, while lower temperatures require longer exposure times. While temperature is the trigger for bleaching, light also influences the severity of bleaching impacts (Jones et al 1998), the consequence being that long, still, cloudless periods in areas affected by anomalously warm temperatures are often the worst affected by bleaching.

Bleached corals are still living and, if stressful conditions subside soon enough, zooxanthellae can repopulate their tissues and the corals can survive the bleaching event. However, even corals that survive are likely to experience reduced growth rates (Goreau and Macfarlane 1990), decreased reproductive capacity (Ward and Harrison 2000), and increased susceptibility to disease (Harvell et al 1999). During a bleaching event, exposure to other stressors, such as pathogens, contaminants or sedimentation, can significantly exacerbate the impacts of coral bleaching.

An important synergy exists between bleaching stress and water quality. Degraded water quality affects various life stages of corals, including the health of established colonies and the success of larval recruitment (McClanahan 2002). In light of these implications, consideration should always be given to limiting particular coastal activities during periods of increased temperature stress. This reduces the risk of damage to coral communities that could result from negative interactions between stressors such as turbidity and temperature. Such a strategy could also reduce the risk that developers will be held responsible for any coral mortality that could be due to bleaching.

**A guideline trigger level for sea temperature is set at increases of no more than 1°C above the long-term average maximum.**

### 6.4 *Pesticides*

The use of pesticides (herbicides, insecticides, and fungicides) in Great Barrier Reef catchments has increased progressively in areas under crop cultivation (Hamilton and Haydon 1996). Seven main herbicides are in widespread use throughout the Great Barrier Reef catchment and are being widely detected in fresh and marine waters of the Great Barrier Reef region. The herbicides are diuron, atrazine, ametryn, simazine, hexazinone, 2,4 -D, and tebuthiuron (Klumpp and Westernhagen 1995, Noble et al 1996, Haynes et al 2000ab, McMahon et al 2003, 2005; Duke et al 2005, Mitchell et al 2005, Douglas et al 2005, Rohde et al 2005, Shaw and Muller 2005, Faithful et al 2007, Lewis et al 2007, Prange et al 2007, Prange 2008).

Variable pesticide concentrations in the water are a consequence of many factors including:

- Catchment proximity to the system
- Intensity and methods of application
- Sorption and partitioning coefficients of the pesticide
- Chemical, physical, and microbial breakdown rates
- Temperature of the system
- History of flushing events (Hamilton and Haydon 1996, McMahon et al 2003)

Muller et al (2000) concluded that herbicides, particularly diuron, atrazine and ametryn, are the most likely contaminants to reach the marine environment of those currently in use. These herbicides have relatively long half-lives, high water solubility, and are found in the sediment at high concentrations. The climate of the growing regions and proximity to the water body contribute to their potential to contaminate.

Although banned since the late 1980s, persistent organochlorine compounds have been detected in waters and marine biota in Australia (Kurtz and Atlas 1990, Kannan et al 1995, Klumpp and von Westernhagen 1995, Moss and Mortimer 1996, Haynes et al 2000b). They were applied to control weeds and insects in agriculture and had a number of urban applications (Hamdorf 1992, Klumpp and von Westernhagen 1995). At this stage, a guideline has not been proposed for organochlorine compounds. Comparison of results from earlier studies suggests levels of DDT/DDE ratios are dropping which is consistent with discontinuation of use. Management strategies that minimise the release of other contaminants to the freshwater and marine environment will also work to minimise organochlorine release.

Concentrations of herbicides detected in Great Barrier Reef waters sometimes exceed biological effect levels for marine organisms. While it is not certain that exposure to herbicides is causing ecosystem level environmental effects, sufficient concern exists to warrant establishment of guideline trigger value concentrations, environmental monitoring, and ongoing management to minimise the release of these contaminants to freshwater and marine environments.

Several keystone marine organisms of the Great Barrier Reef including corals (Jones and Kerswell 2003, Jones et al 2003, Owen et al 2003, Råberg et al 2003, Jones 2004, Negri et al 2005, Markey et al 2007), seagrass (Haynes et al 2000b, Ralph 2000, Macinnis–Ng and Ralph 2003, Chesworth et al 2004), mangroves (Duke et al 2003, Bell and Duke 2005) and algae (Schreiber et al 2002, Harrington et al 2005, Bengston Nash et al 2005ab, Magnusson et al 2006, Seery et al 2006) are sensitive to herbicides that are currently applied within Great Barrier Reef catchments.

Contaminants can affect corals in a variety of ways including reduction of photosynthesis in zooxanthellae (Jones and Kerswell 2003, Owen et al 2003, Negri et al 2005), reduced fertilisation and metamorphosis (Mercurio et al 2004, Markey et al 2007), and by causing expulsion of zooxanthellae (Jones and Kerswell 2003, Jones et al 2003, Markey et al 2007). As most adult corals rely on symbiotic dinoflagellates to provide additional energy requirements for colony functioning, this may result in a loss of fitness in the host coral polyp (Jones et al 2003). Pesticides may also impact directly on the physiology of corals. Insecticides are more likely to be the causative agent for this toxicity than herbicides.

Sublethal effects have not been included in derivations of guideline trigger values. However, these responses may be an indicator of sublethal impacts the minimisation of which could prove critical to the protection of the ecosystem. Discussion of sublethal effects is presented in section 6.6. Further research on the importance of these responses is recommended.

The aim of the Great Barrier Reef Marine Park Authority is the long-term protection and maintenance of the Great Barrier Reef Marine Park and World Heritage Area. In considering the establishment of trigger values, for pesticides (and the one biocide derived), concentrations protective of 99, 95 and 90 per cent of species have been calculated.

For high ecological value water bodies, a guideline concentration that is protective of 99 per cent of species is ideal. In section 1.3, the environmental values of the Great Barrier Reef Marine Park were discussed. Regardless of the current condition of the waters (high ecological value, slightly to moderately disturbed or highly disturbed), aquatic ecosystem protection is the environmental value currently applied to the entire World Heritage Area. The trigger value applies regardless of the current condition of the ecosystems. Even in the highly-disturbed trawl grounds any effects of

pesticides and biocides would be unacceptable. Therefore, trigger values for these parameters as derived in these guidelines apply to all of the five water bodies at the derived concentration protective of 99 per cent of species.

In order to ensure the health of the marine ecosystem significant consideration must be given to the preservation of food webs, in particular the primary producers. There is a paucity of data relating to the toxicity of many contaminants to those primary producers in the tropical marine ecosystem. Given the mode of action of many of the pesticides it is possible that a higher weighting should be given to effect responses that occur in plants rather than in animals. At present, no weighting is applied in the statistical distribution application and so the data will tend to be biased, which in practice tends to be towards the more acute mortality endpoints on animals such as fish and crustaceans that require extrapolation to chronic effects.

Finally, additive, synergistic and antagonistic effects can complicate the setting of guideline trigger values, and are still poorly understood.

Time of exposure to contaminants is important, as the early life stages of corals are most at risk from herbicides. Spawning generally occurs around November to December each year, a time that often coincides with wet season rainfall and subsequent high run-off events containing concentrated pulses of contaminants. Added stressors such as high water temperatures and low salinity at this time when the highest herbicide concentrations are likely to reach the marine environment increase the concern for the ongoing health of the ecosystems (Haynes et al 2000b).

#### 6.4.1 Diuron

The ANZECC and ARMCANZ (2000) water quality guideline database for toxicants (Sunderam et al 2000) (Table 4) has two marine data sets reported for diuron.

Table 4: Marine data sets for diuron (Sunderam et al 2000)

| Species  | Effect conc.<br>µg/L | Endpoint  | Toxicity measure |
|--|----------------------|-----------|------------------|
| <b><i>Fish</i></b>                               |                      |           |                  |
| <i>Mugil curema</i> (white mullet)               | 6300                 | Mortality | LC50, 48h Acute  |
| <b><i>Invertebrates</i></b>                      |                      |           |                  |
| <i>Crassostrea virginica</i><br>(eastern oyster) | 3200                 | Growth    | LC50, 96h Acute  |

The following marine data have been extracted from the Australian Pesticides and Veterinary Medicines Authority (APVMA 2005) preliminary review findings for diuron, Volume I and II (Table 5). This review relies largely on data from the US Environmental Protection Agency Pesticide Ecotoxicity Database, current as of March 2002 (US Environmental Protection Agency, 2004). The number of studies and taxonomic groups represented by the data provide sufficient information to develop a formal guideline.

The same data have been used by the US Environmental Protection Agency in their Re-registration Eligibility Document (RED) for diuron, which is publicly available (US Environmental Protection Agency 2003). As these guidelines derive trigger values for management action it was considered appropriate to use all of the available scientifically sound data.

Table 5: APVMA 2005 ecotoxicity testing for effects of diuron

| Organisms and comments  | Toxicity, µg/L<br>test substance<br>(95% CL) | Year<br>reported | US EPA<br>category |
|---|--|------------------|--------------------|
| <b><i>Fish</i></b>  |  |                  |                    |
| Striped mullet ( <i>Mugil cephalus</i> )<br>tech. (95%) static                                    | 6300 (NR)<br>48h, acute                      | 1986             | S                  |
| Sheepshead minnow ( <i>Cyprinodon variegatus</i> )<br>99% active constituent; static              | 6700 (NR)<br>96h acute<br>NOEC = 3600        | 1986             | Core               |
| <b><i>Invertebrates</i></b>   |  |                  |                    |
| Mysid shrimp ( <i>Mysidopsis bahia</i> )<br>99% active constituent; static                        | LC50 = 1100<br>96h acute<br>NOEC = 1000      | 1987             | Core               |
| Mysid shrimp ( <i>Mysidopsis bahia</i> )<br>96.8% active constituent; early life stage,<br>static | 28d LOEC =<br>560<br>NOEC = 270              | 1992             | Core               |
| Brown shrimp ( <i>Penaeus aztecus</i> )<br>95% active constituent; flow-through                   | LC50 = 1000<br>48h acute                     | 1986             | S                  |
| Eastern oyster ( <i>Crassostrea virginica</i> )<br>96.8% active constituent; flow-through         | EC50 = 4800<br>96h acute<br>NOEC = 2400      | 1991             | Core               |
| Eastern oyster<br>( <i>Crassostrea virginica</i> ); 96.8% active<br>constituent; flow-through     | EC50 = 3200<br>96h acute                     | 1986             | Core               |
| <b><i>Algae</i></b>   |  |                  |                    |
| <i>Dunaliella tertiolecta</i> 95% active constituent<br>static                                    | EC50 = 20<br>240h chronic                    | 1986             | S                  |
| <i>Platymonas</i> sp. 95% active<br>constituent static  | EC50 = 17<br>72h chronic                     | 1986             | S                  |
| <i>Porphyridium cruentum</i> (red algae)<br>95% active constituent static                         | EC50 = 24<br>72h chronic                     | 1986             | S                  |
| <i>Monochrysis lutheri</i><br>95% active constituent static                                       | EC50 = 18<br>72h chronic                     | 1986             | S                  |
| <i>Isochrysis galbana</i><br>95% active constituent static  | EC50 = 10<br>72h chronic                     | 1986             | S                  |
| <b><i>Marine diatoms</i></b>  |  |                  |                    |
| <i>Navicula incerta</i> 95% active<br>constituent static  | EC50 = 93<br>72h chronic                     | 1986             | S                  |
| <i>Nitzschia closterium</i> 95% active constituent<br>static                                      | EC50 = 50<br>72h chronic                     | 1986             | S                  |
| <i>Phaeodactylum tricornutum</i><br>95% active constituent static                                 | EC50 = 10<br>240h chronic                    | 1986             | S                  |
| <i>Stauroneis amphoroidea</i><br>95% active constituent static                                    | EC50 = 31<br>72h chronic                     | 1986             | S                  |
| <i>Thalassiosira fluviatilis</i><br>95% active constituent static                                 | EC50 = 95<br>72h chronic                     | 1986             | S                  |
| <i>Cyclotella nana</i><br>95% active constituent static   | EC50 = 39<br>72h chronic                     | 1986             | S                  |
| <i>Amphora exigua</i><br>95% active constituent static  | EC50 = 31<br>72h chronic                     | 1986             | S                  |



The minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups was met, so the BurrliOZ statistical distribution method (Campbell et al 2000) was used to derive a guideline trigger value for ecosystem protection. An assessment factor of 10 was applied to convert acute LC or EC50s to chronic NOECs, and a factor of 5 to convert chronic EC/IC50s to chronic NOECs. The endpoint values were entered into the BurrliOZ statistical distribution software (Campbell et al 2000) to determine a concentration protective of 99, 95 and 90 per cent of species. Where two toxicity values were reported for the same endpoint in the same species (eastern oyster) the geometric mean of the two results was entered (Van de Plassche et al 1995).

**Moderate reliability guideline trigger values of 0.9, 1.6 and 2.3 µg/L have been derived for diuron for protection of 99, 95 and 90 per cent of species respectively.**

#### 6.4.2 Atrazine

The National Registration Authority for Agricultural and Veterinary Chemicals, Australia, reviewed the registration of atrazine in 1997 (NRA 1997). The review has five marine data sets for atrazine (Table 6). The review found that atrazine showed continued potential to contaminate ground and surface waters and that some safety margins were narrow. Recommendations were made to reduce aquatic contamination, and to conduct monitoring to trace effects and strategy effectiveness. The review quotes the threshold for aquatic ecosystem effects at about 20 µg/L for the Australian aquatic environment. Drinking water quality is quoted at around 0.5 µg/L. However, the issue of including certain metabolites of atrazine is raised and the suggestion is that doing so would lower the guideline value.

Table 6: The NRA Review 1997 ecotoxicity data for effects of atrazine

| Species   | Effect conc.<br>µg/L | Endpoint  | Toxicity measure |
|---|----------------------|-----------|------------------|
| <b><i>Fish</i></b>                                  |                      |           |                  |
| <i>Cyprinodon variegatus</i><br>(sheepshead minnow) | 19 000               | Mortality | LC50, Acute      |
| <b><i>Crustaceans</i></b>                           |                      |           |                  |
| <i>Acartia tonsa</i><br>(calanoid copepod)          | 94<br>4300           | Mortality | LC50, Acute      |
| <i>Mysidopsis bahia</i><br>(opossum shrimp)         | 5400                 | Mortality | LC50, Acute      |
| <b><i>Diatom</i></b>                                |                      |           |                  |
| <i>Skeletonema costatum</i>                         | 55                   | Growth    | LC50, Acute      |
| <b><i>Algae</i></b>                                 |                      |           |                  |
| <i>Dunaliella tertiolecta</i>                       | 170                  | Growth    | LC50, Acute      |

The ANZECC and ARMCANZ water quality guideline database for toxicants (Sunderam et al 2000) (Table 7) has fourteen marine data sets reported for atrazine.

Table 7: Marine data sets for atrazine (Sunderam et al 2000)

| Species   | Effect conc.<br>µg/L | Endpoint  | Toxicity measure |
|---|----------------------|-----------|------------------|
| <b><i>Fish</i></b>                                  |                      |           |                  |
| <i>Cyprinodon variegatus</i><br>(sheepshead minnow) | 2300                 | Mortality | LC50, Acute, 96h |
| <i>Cyprinodon variegatus</i>                        | 2000                 | Mortality | LC50, Acute, 96h |

| Species   | Effect conc.<br>µg/L | Endpoint  | Toxicity measure    |
|---|----------------------|-----------|---------------------|
| <i>Cyprinodon variegatus</i>                      | 16 200               | Mortality | LC50, Acute, 96h    |
| <i>Leiostomus xanthurus</i><br>(spot)             | 8500                 | Mortality | LC50, Acute, 96h    |
| <b>Crustaceans</b>                                |                      |           |                     |
| <i>Acartia tonsa</i><br>(calanoid copepod)        | 94                   | Mortality | LC50, Acute, 96h    |
| <i>Eurytemora affinis</i><br>(calanoid copepod)   | 2600                 | Mortality | LC50, Acute, 96h    |
| <i>Eurytemora affinis</i>                         | 13 200               | Mortality | LC50, Acute, 96h    |
| <i>Eurytemora affinis</i>                         | 500                  | Mortality | LC50, Acute, 96h    |
| <i>Mysidopsis bahia</i><br>(opossum shrimp)       | 5400                 | Mortality | LC50, Acute, 96h    |
| <i>Mysidopsis bahia</i>                           | 1000                 | Mortality | LC50, Acute, 96h    |
| <i>Penaus duorarum</i><br>(pink shrimp (america)) | 6900                 | Mortality | LC50, Acute, 96h    |
| <i>Eurytemora affinis</i><br>(calanoid copepod)   | 17 500               | Mortality | NOEC, Chronic, 192h |
| <i>Eurytemora affinis</i>                         | 4200                 | Mortality | NOEC, Chronic, 192h |
| <i>Eurytemora affinis</i>                         | 12 250               | Mortality | NOEC, Chronic, 192h |

The Society of Environmental Toxicology and Chemistry (SETAC 2005) published a book on a probabilistic aquatic ecological risk assessment of atrazine in northern American surface waters in 2005 that included additional marine data sets for atrazine (Table 8). Toxicity data published prior to 1980 were not included, as they were considered to be unreliable due to advances in experimental and analytical capabilities since that time (Warne 1998).

Table 8: Marine data sets for toxicity effects of atrazine (SETAC)

| Species                                     | Effect conc.<br>µg/L | Endpoint  | Toxicity measure   | Reference                   |
|---|----------------------|-----------|--------------------|-----------------------------|
| <b>Crustaceans</b>                          |                      |           |                    |                             |
| <i>Palaemonetes pugio</i><br>(grass shrimp) | 9000                 | Mortality | LC50<br>Acute, 96h | Ward and<br>Ballantine 1985 |
| <i>Tigriopus brevicornis</i><br>(copepod)   | 121                  | Mortality | LC50<br>Acute      | Forget et al 1998           |
| <b>Diatom</b>                               |                      |           |                    |                             |
| <i>Skeletonema costatum</i>                 | 50                   | Growth    | EC50, Acute        | Walsh et al 1988            |
| <i>Minutocellus polymorphos</i> *           | 20                   | Growth    | EC50, Acute        | Walsh et al 1988            |
| <i>Skeletonema costatum</i>                 | 24                   | NR        | EC50               | US EPA 2002                 |
| <b>Algae</b>                                |                      |           |                    |                             |
| <i>Dunaliella tertiolecta</i>               | 170                  | Growth    | EC50, chronic      | Hughes et al 1988           |

\* This test was not included in the SETAC publication but was conducted in the same manner as the *Skeletonema sp* test and therefore is added here.

The following data published in SETAC 2005 were not used in the derivation of the trigger value (Table 9). For *Cyprinodon variegatus* an LC50 was unobtainable (reported as greater than 16 000) then the NOEC was calculated from this using an assessment factor estimate. For *Crassostrea virginica* the same applies (although the LC50 was reported as greater than 30 000). There is no need to use 'greater than' data when there is sufficient measured data available, so this data has been excluded. In addition, a more stringent assessment factor for atrazine conversion from acute to chronic toxicity has been determined.

The *Mysidopsis bahia* effect concentration appears to have been misreported from the original paper. The effect concentration is 94 µg/L and this is the same test as reported in Table 7.

The *Phaeodactylum tricornutum* test was conducted in freshwater medium and is therefore, in accordance with the ANZECC and ARMICANZ (2000) derivation procedures, not used in deriving the marine trigger value.

The copepod work referenced to Thursby et al 1990, the algal work of Thursby and Tagliabue 1990, and the Hoberg 1993c are not scientific publications and are therefore excluded.

Only a bibliographic citation was able to be retrieved on the Mayer 1987 reference. The description advises that acute toxicity data since 1961 were evaluated for quality and a database established. Test methodology was not able to be confirmed and the data was excluded. It is expected that much of the testing would have been pre-1980 and therefore would also have been excluded under the Warne (1998) provision. Inclusion of the data in the BurrliOZ run resulted in a derived trigger value in the same order of magnitude.

The *Potamogeton pectinatus* tests were conducted in salinities between 1 and 12 parts per thousand, are therefore not considered to be marine data, and are not used in deriving the marine trigger value.

The Malcolm Pirnie 1986 work was not referenced in the book and was unable to be found in google scholar searches or other library research.

Table 9: Excluded SETAC 2005 atrazine toxicity data

| Species   | Effect conc.<br>µg/L | Endpoint  | Toxicity<br>measure  | Reference              |
|---|----------------------|-----------|----------------------|------------------------|
| <b><i>Fish</i></b>  |                      |           |                      |                        |
| <i>Cyprinodon variegatus</i><br>(sheepshead minnow,<br>embryo-juvenile) | 1789                 | Mortality | NOEC                 | Ward & Ballantine 1985 |
| <b><i>Mollusc</i></b>   |                      |           |                      |                        |
| <i>Crassostrea virginica</i><br>(eastern oyster, embryo)                | 30 000               | Mortality | LC50<br>Acute        | Ward & Ballantine 1985 |
| <b><i>Crustaceans</i></b>   |                      |           |                      |                        |
| <i>Mysidopsis bahia</i><br>(opossum shrimp)                             | 920                  | Mortality | LC50<br>chronic, 28d | Ward & Ballantine 1985 |
| <i>Acartia clausii</i><br>(copepod)                                     | 7945                 | Mortality | LC50<br>Acute        | Thursby et al 1990     |
| <i>Acartia tonsa</i><br>(copepod)                                       | 92                   | Mortality | LC50<br>Acute        | Thursby et al 1990     |
| <i>Penaus aztecus</i><br>(brown shrimp)                                 | 1000                 | Mortality | LC50,<br>Acute, 48h  | Mayer 1987             |
| <b><i>Diatom</i></b>  |                      |           |                      |                        |
| <i>Phaeodactylum</i><br><i>tricornutum</i>                              | 15                   | Growth    | NOEC                 | Mayasich et al 1987    |
| <i>Skeletonema costatum</i>   | 260                  |           | EC50, Acute          | Mayer 1987             |
| <i>Skeletonema costatum</i>   | 14                   |           | NOEC                 | Hoberg 1993c           |
| <b><i>Algae</i></b>   |                      |           |                      |                        |
| <i>Potamogeton pectinatus</i><br>(sago)                                 | 7.5                  |           | NOEC                 | Hall et al 1997        |

|  |      |  |               |                            |
|--|------|--|---------------|----------------------------|
| <i>Laminaria saccharina</i><br>(brown algae) | 33.2 |  | NOEC          | Thursby and Tagliabue 1990 |
| <i>D. tertiolecta</i>                        | 170  |  | EC50, chronic | Malcolm Pirnie 1986        |
| <i>Chlamydomonas</i> sp<br>(green algae)     | 60   |  | EC50 Acute    | Mayer 1987                 |
| <i>Platymonas</i> sp                         | 102  |  | EC50, Acute   | Mayer 1987                 |
| <i>Chlorella</i> sp                          | 143  |  | EC50, Acute   | Mayer 1987                 |
| <i>D. tertiolecta</i>                        | 300  |  | EC50, chronic | Mayer 1987                 |

Since the publication of the book a further publication on the effects of atrazine on marine species has become available and is reported here for inclusion in the derivation (Table 10).

Table 10: Additional marine data on toxicity effects of atrazine

| Species                          | Effect conc.<br>µg/L | Endpoint | Toxicity measure  | Reference         |
|----------------------------------|----------------------|----------|-------------------|-------------------|
| <b><i>Phytoplankton</i></b>      |                      |          |                   |                   |
| <i>Dunaliella tertiolecta</i>    | 69                   | Growth   | EC50 Chronic, 96h | Weiner et al 2004 |
| <i>Phaeodactylum tricornutum</i> | 61                   | Growth   | EC50 Chronic, 96h | Weiner et al 2004 |
| <i>Synechococcus</i> sp          | 44                   | Growth   | EC50 Chronic, 96h | Weiner et al 2004 |
| <i>Isochrysis galbana</i>        | 91                   | Growth   | EC50 Chronic, 96h | Weiner et al 2004 |

The minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups was met, so the BurliOZ statistical distribution method (Campbell et al 2000) was used to derive a guideline trigger value for ecosystem protection. Combining the accepted data sets above provides at least five acute LC50 values. The geometric mean of the chronic NOECs for the copepod *Eurytemora affinis* was entered in preference to the acute to chronic converted LC50 value. Where more than one toxicity value was reported for the same endpoint in the same species the geometric mean of the values was used (Van de Plassche et al 1995). An assessment factor of 20.21 was applied to convert acute EC/LC50 data to chronic NOEC data. A modified van de Plassche et al (1993) scheme applied in the ANZECC and ARMCANZ (2000) guidelines recommends an assessment factor of five be applied to convert a chronic EC/LC50 effect to a chronic NOEC, and this was applied to the chronic EC50 data where there was no acute EC50 data. The endpoint values were entered into the BurliOZ statistical distribution software (Campbell et al 2000) to determine a concentration protective of 99, 95 and 90 per cent of species.

**Moderate reliability guideline trigger values of 0.6, 1.4 and 2.5 µg/L have been derived for atrazine for the protection of 95 and 90 per cent of species respectively.**

#### 6.4.3 Ametryn

The ANZECC and ARMCANZ water quality guideline database for toxicants (Sunderam et al 2000) has no marine or freshwater data sets for ametryn. Data on effects on marine species is available from the US Environmental Protection Agency Pesticide Ecotoxicity Database, current as of March 2002 (US Environmental Protection Agency, 2004, Table 11).

Table 11: US EPA toxicity data for ametryn

| Organisms and comments  | Toxicity, µg/L<br>test substance<br>(95% CL) | Year<br>reported | US EPA<br>category          |
|---|--|------------------|-----------------------------|
| <b><i>Fish</i></b>  |  |                  |                             |
| Sheepshead minnow ( <i>Cyprinodon variegates</i> ) 96.7% active constituent; static                       | LC50 = 5800<br>acute, 96h<br>NOEC = 2800     | 1989             | Core                        |
| <b><i>Invertebrates</i></b>   |  |                  |                             |
| Mysid shrimp ( <i>Mysidopsis bahia</i> ) 96.7% active constituent; juvenile mysid static                  | LC50 = 2300<br>(1700-2900)<br>acute, 96h     | 1989             | Core                        |
| Quahog clam ( <i>Mercenaria mercenaria</i> ) 96.7% active constituent; embryo/larvae, static              | EC50 = 11000<br>Acute, 48h                   | 1989             | S                           |
| Brine shrimp ( <i>Artemia salina</i> ), active constituent – instar II-III larvae, multiwell test at 25°C | EC50 = 33000<br>Acute, 24h                   | 1995             | Not standard<br>US EPA test |
| <b><i>Diatoms</i></b>   |  |                  |                             |
| <i>Acanthes brevipes</i> , 100% active constituent  | EC50 = 19<br>Chronic, 72h                    | 1986             | S                           |
| <i>Navicula incerta</i> , 100% active constituent   | EC50 = 97<br>Chronic, 72h                    | 1986             | S                           |
| <i>Nitzschia closterium</i> 100% active constituent static  | EC50 = 62<br>Chronic, 72h                    | 1986             | S                           |
| <i>Phaeodactylum tricornutum</i> 100% active constituent static   | EC50 = 20<br>Chronic, 240h                   | 1986             | S                           |
| <i>Stauroneis amphoroides</i> 100% active constituent static  | EC50 = 26<br>Chronic, 72h                    | 1986             | S                           |
| <i>Thalassiosira guillardii</i> 100% active constituent static  | EC50 = 55<br>Chronic, 72h                    | 1986             | S                           |
| <b><i>Algae (green)</i></b>   |  |                  |                             |
| <i>Neochloris</i> sp. 100% active constituent static  | EC50=36<br>Chronic, 72h                      | 1986             | S                           |
| <i>Platymonas</i> sp. 100% active constituent   | EC50 = 24<br>Chronic, 72h                    | 1986             | S                           |
| <b><i>Algae (brown)</i></b>   |  |                  |                             |
| <i>Isochrysis galbana</i> 100% active constituent static  | EC50 = 10<br>Chronic, 240h                   | 1986             | S                           |
| <i>Dunaliella tertiolecta</i> , 80WP  | EC50 = 20<br>Chronic, 240h                   | 1986             | S                           |

The minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups was met, so the BurrliOZ statistical distribution method (Campbell et al 2000) was used to derive a guideline trigger value for ecosystem protection. The software does warn however that the number of data are small and that results should be interpreted with caution. As trigger values the authors consider it reasonable to use the results.

Where a NOEC was reported for a species this was used in preference to converting acute to chronic toxicity measures. There is no acute to chronic assessment factor for ametryn and therefore the assessment factor of 10 was applied to convert acute LC or EC50s to chronic

NOECs, and a factor of five to convert chronic EC/IC50s to chronic NOECs. The endpoint values were entered into the BurrliOZ statistical distribution software (Campbell et al 2000) to determine a concentration protective of 99, 95 and 90 per cent of species.

**Moderate reliability guideline trigger values of 0.5, 1.0 and 1.6 µg/L** have been derived for **ametryn** for protection of 99, 95 and 90 per cent of species respectively.

#### 6.4.4 Simazine

The ANZECC and ARMCANZ water quality guideline database for toxicants (Sunderam et al 2000) has no marine data sets for simazine. In the absence of marine data the moderate reliability freshwater guideline concentration was applied with a low reliability. These are 0.2, 3.2 and 11 µg/L respectively, for protection of 99, 95 and 90 per cent of species.

Since the publication of ANZECC and ARMCANZ (2000) data on effects on marine species has become available from the US Environmental Protection Agency under their Endangered Species Effects Determinations and Consultations documentation. Data for simazine is from 2003. The acute toxicity data for estuarine and marine organisms are mostly 'greater than' data that do not provide information that can be used in a derivation exercise. There is data for one invertebrate shrimp and several aquatic plants (Table 12). There are no chronic NOEC toxicity data.

Table 12: US EPA toxicity data for simazine 2003

| Organisms and comments                | Toxicity, µg/L                         | Source |
|---------------------------------------|--|--------|
| <b><i>Invertebrates</i></b>           |  |        |
| <i>Penaeus duorarum</i> (pink shrimp) | LC50=113000<br>acute, 96h<br>98.1 % ai | EFED   |
| <b><i>Aquatic Plants</i></b>          |  |        |
| <i>Isochrysis sp</i>                  | EC50=500<br>Chronic,10 day             | EFED   |
| <i>Phaeodactylum sp.</i>              | EC50 = 500<br>Chronic,10 day           | EFED   |
| <i>Skeletonema sp.</i>                | EC50 = 600<br>Chronic,5 day            | EFED   |
| <i>Dunaliella sp</i>                  | EC50 = 5000<br>Chronic,10 day          | EFED   |

In addition to the data published in the US EPA document the chemical company Syngenta provided the Great Barrier Reef Marine Park Authority with additional test data on two of the aquatic plants (Table 13), and a further study was conducted on the sea bream *Sparus aurata* (Arufe et al 2004: Table 14).

Table 13: Toxicity data for simazine (Syngenta)

| Organisms and comments       | Toxicity, µg/L         | Source   |
|------------------------------|------------------------|----------|
| <b><i>Aquatic Plants</i></b> |                        |          |
| <i>Skeletonema sp.</i>       | EC50 = 1040<br>Chronic | Syngenta |
| <i>Dunaliella sp</i>         | EC50 = 2000<br>Chronic | Syngenta |

Table 14: Toxicity data for simazine 2004

| Species                             | Effect conc.<br>µg/L | Endpoint  | Toxicity<br>measure |
|-------------------------------------|----------------------|-----------|---------------------|
| <b><i>Fish</i></b>                  |                      |           |                     |
| <i>Sparus aurata</i><br>(sea bream) | 4190                 | Mortality | LC50<br>Acute, 72h  |
| <i>Sparus aurata</i>                | 2250                 | Mortality | NOEC                |
| <i>Sparus aurata</i>                | 4500                 | Growth    | NOEC                |

The minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups is not met, so the BurrliOZ statistical distribution method to derive a guideline trigger value cannot be applied. The OECD (1981) approach was not as prescriptive as Warne and specified five data points that represented at least the basic trophic levels: aquatic plants, crustaceans and fish. This less prescriptive test would be met by the data set, although clearly the set is small.

The BurrliOZ statistical distribution method (Campbell et al 2000) was run, although this is not the standard adopted for the derivation of the ANZECC and ARMCANZ (2000) guidelines and the value is provided only out of interest as a comparative. The endpoint values were entered into the BurrliOZ statistical distribution software (Campbell et al 2000) to determine a concentration protective of 99, 95 and 90 per cent of species. A modified van de Plassche et al (1993) scheme applied in the ANZECC and ARMCANZ (2000) guidelines recommends an assessment factor of five be applied to convert a chronic EC/LC50 effect to a chronic NOEC, so this was used. Where two toxicity values were reported for the same endpoint in the same species the geometric mean of the two results was entered (Van de Plassche et al 1995). The NOEC for the seabream mortality test was used in favour of the LC50. The software does warn that the number of data are small and that results should be interpreted with caution. Guideline trigger values of 30, 59 and 88 µg/L result from applying this method.

There are at least three chronic EC50 or LC50 values in the data sets provided. Applying the assessment factor of five as described above but to the lowest of the effects concentrations of the set of three results in a guideline trigger value of 100 µg/L for simazine, which is between one and four orders of magnitude greater than the freshwater guideline adopted by ANZECC and ARMCANZ (2000) depending upon what per cent of species protection is being considered.

If simazine is identified as a contaminant for which greater certainty of the guideline trigger value is required we note that an additional invertebrate toxicity test, preferably a zooplankton to meet the minimum data requirement (Warne 2001), would be of most benefit.

Given the low reliability of any of these derivation methods at this stage, the Great Barrier Reef Marine Park Authority adopts the more conservative ANZECC and ARMCANZ (2000) guideline, applying the moderate reliability freshwater guideline with a low reliability.

**A low reliability guideline trigger value of 0.2, 3.2 and 11 µg/L is applied for simazine for protection of 99, 95 and 90 per cent of species respectively.**

#### 6.4.5 Hexazinone

The ANZECC and ARMCANZ water quality guideline database for toxicants (Sunderam et al 2000) has no marine data sets for hexazinone. A low reliability freshwater guideline was calculated for hexazinone as 75 µg/L.

Since the publication of the ANZECC and ARMCANZ (2000) water quality guideline data on effects on marine species has become available from the US Environmental Protection Agency Pesticide Ecotoxicity Database (US Environmental Protection Agency, 2004, Table 15).

Table 15: US EPA toxicity data for hexazinone

| Organisms and comments                                  | Toxicity, µg/L test substance         | Year reported |
|---|---------------------------------------|---------------|
| <b>Crustacea</b>  |                                       |               |
| <i>Decapoda sp</i> (grass shrimp)                       | LC50 94 000<br>98% ac                 | 1984          |
| <i>Palaeomonetes pugio</i> , (daggerblade grass shrimp) | LC50 78 000<br>95% ac                 | 2000          |
| <b>Mollusca</b>   |                                       |               |
| <i>Crassostrea virginica</i> (eastern oyster)           | LC50=560 000<br>acute, 48h<br>95 % ai | EFED          |
| <i>Crassostrea virginica</i> (eastern oyster)           | LC50=320 000<br>acute, 48h<br>95 % ai | EFED          |
| <b>Diatom</b>   |                                       |               |
| <i>Skeletonema costatum</i>                             | EC50 = 120<br>NOEC = 4                | EFED          |

These data support the ANZECC and ARMCANZ (2000) adopted freshwater guideline concentration. They still provide insufficient data to meet the minimum requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups, so the BurrliOZ statistical distribution method to derive a guideline trigger value cannot be applied.

There are at least three acute EC50 or LC50 values in the data set provided. Therefore the lowest of the acute values is divided by 100 (OECD 1992) to provide a low reliability guideline trigger value of 1.2 µg/L for hexazinone which is over an order of magnitude lower than the freshwater guideline adopted by ANZECC and ARMCANZ (2000).

**A low reliability guideline trigger value of 1.2 µg/L is adopted for hexazinone.**

#### 6.4.6 2,4-D

The ANZECC and ARMCANZ water quality guideline database for toxicants (Sunderam et al 2000) has five marine data reported for 2,4-D (Table 16).

Table 16: Marine data for 2,4-D (Sunderam et al 2000)

| Species                                     | Effects conc. µg/L | Endpoint  | Toxicity measure |
|---|--------------------|-----------|------------------|
| <b>Fish</b>                                 |                    |           |                  |
| <i>Fundulus similis</i> (longnose killfish) | 3000               | Mortality | LC50, Acute, 48h |
| <i>Mugil curema</i> (white mullet)          | 1500               | Mortality | LC50, Acute, 48h |



| Species  | Effects conc.<br>µg/L | Endpoint  | Toxicity measure |
|--|-----------------------|-----------|------------------|
| <b>Crustaceans</b>                                 |                       |           |                  |
| <i>Chasmagnathus granulata</i><br>(crab)           | 6 730 000             | Mortality | LC50, Acute, 72h |
| <i>Chasmagnathus granulata</i>                     | 3 370 000             | Mortality | LC50, Acute, 96h |
| <b>Molluscs</b>                                    |                       |           |                  |
| <i>Mytilus edulis</i><br>(common bay mussel, blue) | 259 000               | Mortality | LC50, Acute, 96h |

Concerns about potential risks to people and to the environment and off-target crops led to the APVMA announcement, in October 2006, of the suspension of products containing high-volatility ester forms of the herbicide 2,4-D <http://www.apvma.gov.au/chemrev/2,4-D.shtml> (accessed 28 Feb 2007).

The APVMA published preliminary review findings in 2006 in relation to approvals for 2,4-D related products (APVMA 2006abcdef). 2,4-D is available in a number of forms and the toxicity of the forms is variable. Endpoint results from the APVMA database are listed for all forms in Table 17. The geometric mean of the effects concentration was used in the BurliOZ (Campbell et al 2000) analysis.

Only the preliminary review findings for high volatile esters had been released at time of writing. The APVMA proposed to find:

*‘ that it is NOT satisfied that continued use ..... would not be likely to have an unintended effect that is harmful to animals, plants or things in the environment. ’*

The preliminary risk assessments for aquatic fish and invertebrate for acid and salt forms was found to be acceptable, but unacceptable for esters. Risk assessments for algae and aquatic plants were unacceptable for all forms.

A refined risk assessment for the high volatile esters considered the risks from broadcast and non-broadcast use to be acceptable. Direct application of 2,4-D esters in aquatic situations was found to have unacceptable risk. Short chain high volatile ester forms have been recommended for discontinuation because of their increased risks.

Ester forms are identified as having higher toxicity to marine species than other forms. Several forms of ester are included in the reports. Two of the forms, butoxyethyl and isopropyl, are not used in Australia and their endpoint toxicity results have been excluded. The acid form is not as soluble as salt or ester forms and as such is not used as often commercially. Evidence in the literature indicates that amine salts are not persistent under most environmental conditions, dissociating rapidly to the acid equivalent, hence acid data may be used to characterise the risk to marine fish.

Table 17: The APVMA 2006 ecotoxicity data for effects of 2,4-D

| Species  | Effects conc.<br>µg/L                                  | Endpoint  | Toxicity measure |
|--|--|-----------|------------------|
| <b>Fish</b>  |  |           |                  |
| <i>Menidia beryllina</i><br>(tidewater silverside) | 175 000 A<br>469 000 S<br>187 000 S ae<br>203 000 S ae | Mortality | LC50<br>Acute    |

| Species  | Effects conc.<br>µg/L                              | Endpoint             | Toxicity<br>measure |
|--|--|----------------------|---------------------|
| <b><i>Molluscs</i></b>                           |  |                      |                     |
| <i>Crassostrea virginica</i><br>(eastern oyster) | 57 000 A<br>146 000 A<br>136 000 S                 | Growth<br>inhibition | EC50<br>Acute       |
| <b><i>Crustaceans</i></b>                        |  |                      |                     |
| <i>Penaeus duorarum</i><br>(pink shrimp)         | 554 000 A<br>150 000 S                             | Mortality            | LC50<br>Acute       |
| <b><i>Diatoms</i></b>                            |  |                      |                     |
| <i>Skeletonema costatum</i>                      | 150 E <sup>*</sup> ae<br>129 000 S ae <sup>+</sup> | Growth<br>inhibition | LC50<br>Acute       |

A = acid form; E = ester form; S= salt form

<sup>\*</sup> Authors do report issues analysing this result with nominal concentrations overestimating actual exposures

<sup>+</sup> A plotted equation effects concentration

ae = acid equivalent

By combining the data in the two tables above the minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups is met, so the BurrliOZ statistical distribution method (Campbell et al 2000) can be used to derive a guideline trigger value for ecosystem protection. The software does warn however that the number of data are small and that results should be interpreted with caution. As trigger values the authors consider it reasonable to use the results.

An assessment factor of 10.22 was applied for conversion of acute data to chronic NOECs. Where more than one toxicity value was reported for the same endpoint in the same species the geometric mean of the values was entered (Van de Plassche et al 1995). The effect concentration values were entered into the BurrliOZ statistical distribution software (Campbell et al 2000) to determine a concentration protective of 99, 95 and 90 per cent of species.

**Moderate reliability guideline trigger values of 0.8, 30.8 and 152 µg/L were derived for 2,4- D for protection of 99, 95 and 90 per cent of species respectively.**

#### 6.4.7 Tebuthiuron

The ANZECC and ARMCANZ water quality guideline database for toxicants (Sunderam et al 2000) has three marine data reported for tebuthiuron (Table 18).

Table 18: Marine data sets for tebuthiuron (Sunderam et al 2000)

| Species                                  | Effects conc.<br>µg/L | Endpoint  | Toxicity measure |
|--|-----------------------|-----------|------------------|
| <b><i>Crustaceans</i></b>                |                       |           |                  |
| <i>Penaeus duorarum</i><br>(pink shrimp) | 84 000                | Mortality | LC50, Acute, 48h |
| <i>Penaeus duorarum</i>                  | 48 000                | Mortality | LC50, Acute, 96h |
| <b><i>Diatom</i></b>                     |                       |           |                  |
| <i>Skeletonema costatum</i><br>(diatom)  | 38                    | Growth    | NOEC, Acute      |

With the limited marine data available, the high reliability freshwater guideline concentrations were adopted in the ANZECC and ARMCANZ (2000) guidelines as low reliability guideline of 0.02, 2 and 20 µg/L respectively for protection of 99, 95 and 90 per cent of species.

A low reliability guideline trigger values of 0.02, 2 and 20 µg/L is applied for tebuthiuron for protection of 99,95 and 90 per cent of species respectively.

#### 6.4.8 Chlorpyrifos / Oxon

The ANZECC and ARMCANZ water quality guideline database for toxicants (Sunderam et al 2000) has more than 45 marine data sets reported for chlorpyrifos (Table 19). The ANZECC and ARMCANZ (2000) guidelines derive high reliability trigger values for marine water for chlorpyrifos of 0.0005, 0.009 and 0.04 µg/L respectively for protection of 99, 95 and 90 per cent of species.

Table 19: Marine data for chlorpyrifos (Sunderam et al 2000)

| Species  | Geometric mean of Effects conc. µg/L | Endpoint       | Toxicity measure |
|--|--------------------------------------|----------------|------------------|
| <b>Fish</b>  |                                      |                |                  |
| <i>Atherinops affinis</i> (topsmelt)                 | 5.0                                  | Mortality      | LC50, Acute      |
| <i>Cyprinodon variegatus</i> (sheepshead minnow)     | 185                                  | Mortality      | LC50, Acute      |
| <i>Fundulus grandis</i> (gulf killifish)             | 1.8                                  | Mortality      | LC50, Acute      |
| <i>Fundulus heteroclitus</i> (mummichog)             | 4.7                                  | Mortality      | LC50, Acute      |
| <i>Fundulus similis</i> (longnose killifish)         | 3.7                                  | Mortality      | LC50, Acute      |
| <i>Fundulus sp.</i>                                  | 470                                  | Mortality      | LC50, Acute      |
| <i>Leiostomus xanthurus</i> (spot)                   | 7.0                                  | Mortality      | LC50, Acute      |
| <i>Leuresthes tenuis</i> (California grunion)        | 1.9                                  | Mortality      | LC50, Acute      |
| <i>Menidia beryllina</i> (inland silverside)         | 5.0                                  | Mortality      | LC50, Acute      |
| <i>Menidia menidia</i> (atlantic silverside)         | 1.9                                  | Mortality      | LC50, Acute      |
| <i>Menidia peninsulae</i> (tidewater silverside)     | 1.3                                  | Mortality      | LC50, Acute      |
| <i>Mugil cephalus</i> (striped mullet)               | 5.4                                  | Mortality      | LC50, Acute      |
| <i>Opsanus beta</i> (gulf toadfish)                  | 263.9                                | Mortality      | LC50, Acute      |
| <b>Crustaceans</b>                                   |                                      |                |                  |
| <i>Ampelisca abdita</i> (amphipod)                   | 0.39                                 | Mortality      | LC50, Acute      |
| <i>Callinectes sapidus</i> (blue crab)               | 5.2                                  | Immobilisation | EC50, Acute      |
| <i>Mysidopsis bahia</i> (opossum shrimp)             | 0.04                                 | Mortality      | LC50, Acute      |
| <i>Palaemonetes pugio</i> (daggerblade grass shrimp) | 1.5                                  | Immobilisation | EC50, Acute      |
| <i>Palaemonetes pugio</i>                            | 1.7                                  | Mortality      | LC50, Acute      |
| <i>Penaus aztecus</i> (brown shrimp)                 | 0.2                                  | Mortality      | EC50, Acute      |

| Species  | Geometric mean of Effects conc.<br>µg/L | Endpoint       | Toxicity measure |
|--|---|----------------|------------------|
| <i>Penaeus duorarum</i><br>(pink shrimp)                   | 2.4                                     | Mortality      | EC50, Acute      |
| <i>Rhepoxynius abronius</i><br>(amphipod)                  | 0.1                                     | Immobilisation | EC50, Acute      |
| <i>Rhepoxynius abronius</i>                                | 0.1                                     | Mortality      | LC50, Acute      |
| <b>Mollusc</b>   |   |                |                  |
| <i>Crassostrea gigas</i><br>(pacific oyster)               | 2000                                    | Developmental  | EC50, Acute      |
| <i>Crassostrea gigas</i>                                   | 95.8                                    | Growth         | EC50, Acute      |
| <i>Mytilus galloprovincialis</i><br>(Mediterranean mussel) | 22 500                                  | Mortality      | LC50, Acute      |
| <b>Green algae</b>   |   |                |                  |
| <i>Chlorococcum sp.</i><br>(green algae)                   | 2000                                    | Growth         | NOEC, Acute      |
| <b>Diatoms</b>   |   |                |                  |
| <i>Amphiprora sp.</i>                                      | 2000                                    | Growth         | NOEC, Acute      |
| <i>Amphora coffeaeformis</i>                               | 10 000                                  | Growth         | NOEC, Acute      |
| <i>Nitzschia closterium</i>                                | 10 000                                  | Growth         | NOEC, Acute      |
| <i>Skeletonema costatum</i>                                | 600                                     | Growth         | EC50, Acute      |
| <i>Skeletonema costatum</i>                                | 1200                                    | Growth         | NOEC, Acute      |
| <i>Thalassiosira pseudonana</i>                            | 150                                     | Growth         | EC50, Acute      |
| <b>Dinoflagellates</b>                                     |   |                |                  |
| <i>Gonyaulax sp.</i><br>(dinoflagellate)                   | 2000                                    | Growth         | NOEC, Acute      |
| <b>Fish</b>  |   |                |                  |
| <i>Leuresthes tenuis</i><br>(California grunion)           | 0.4                                     | Mortality      | NOEC, Chronic    |
| <i>Leuresthes tenuis</i>                                   | 0.25                                    | Not recorded   | NOEC, Chronic    |
| <i>Menidia beryllina</i><br>(inland silverside)            | 0.8                                     | Mortality      | NOEC, Chronic    |
| <i>Menidia menidia</i><br>(atlantic silverside)            | 0.3                                     | Mortality      | NOEC, Chronic    |
| <i>Menidia menidia</i>                                     | 0.3                                     | Not recorded   | NOEC, Chronic    |
| <i>Menidia peninsulae</i>                                  | 0.4                                     | Mortality      | NOEC, Chronic    |
| <i>Menidia peninsulae</i>                                  | 0.4                                     | Not recorded   | NOEC, Chronic    |
| <i>Opsanus beta</i><br>(gulf toadfish)                     | 8.2                                     | Growth         | LOEC, Chronic    |
| <i>Opsanus beta</i>  | 150                                     | Mortality      | LOEC, Chronic    |
| <i>Opsanus beta</i>  | 1.4                                     | Growth         | NOEC, Chronic    |
| <i>Opsanus beta</i>  | 93                                      | Mortality      | NOEC, Chronic    |
| <b>Crustacean</b>  |   |                |                  |
| <i>Mysidopsis bahia</i><br>(opossum shrimp)                | 0.003                                   | Reproduction   | NOEC, Chronic    |

### Additional considerations

Additional data on chlorpyrifos toxicity to corals (Te 1998, Markey et al 2007) have become available since the ANZECC and ARMCANZ (2000) guidelines were released (Table 20).

Chlorpyrifos and chlorpyrifos oxon reduced settlement and metamorphosis by greater than 50 per cent in the larvae of *A. millepora* at concentrations of 1.0 and 0.4 µg/L respectively (Markey et al 2007). Mortality of greater than 50 per cent for the coral *P. damicornis* occurred at concentrations of 6 µg/L chlorpyrifos (Te 1998).

Table 20: Biological effects concentrations from direct toxicity testing of chlorpyrifos

| Species                      | Effect conc.<br>µg/L | Endpoint                       | Toxicity<br>measure | Reference         |
|------------------------------|----------------------|--------------------------------|---------------------|-------------------|
| <b><i>Coral</i></b>          |                      |                                |                     |                   |
| <b><i>Coral larvae</i></b>   |                      |                                |                     |                   |
| <i>A. millepora</i>          | 0.4                  | ↓ settlement and metamorphosis | LOEC                | Markey et al 2007 |
| <i>A. millepora</i>          | 1                    | ↓ settlement and metamorphosis | EC50<br>Acute, 18h  | Markey et al 2007 |
| <b><i>Adult colonies</i></b> |                      |                                |                     |                   |
| <i>P. damicornis</i>         | 6                    | ↑ mortality                    | EC50                | Te 1998           |

Adding the two additional mortality and metamorphosis EC50 effects concentrations from reef data resulted in a minor lowering of the ANZECC and ARMCANZ (2000) trigger values giving derivations of 0.002, 0.009 and 0.03 µg/L for protection of 99, 95 and 90 per cent of species respectively.

A high reliability trigger value was derived in the ANZECC and ARMCANZ (2000) guideline for marine water for chlorpyrifos. The concentration including the additional data is in the same order of magnitude, and because of the need for conversion factor application its inclusion would degrade the reliability to a moderate reliability value. Therefore, the Great Barrier Reef Marine Park Authority adopts the high reliability trigger value aligning with the ANZECC and ARMCANZ (2000) guideline.

The **high reliability guideline trigger values of 0.0005, 0.009 and 0.04 µg/L** are applied for chlorpyrifos for protection of 99, 95 and 90 per cent of species respectively.

#### **6.4.9 Endosulfan**

The ANZECC and ARMCANZ water quality guideline database for toxicants (Sunderam et al 2000) has more than 35 marine data sets reported for endosulfan (Table 21). A moderate reliability trigger value for marine water for endosulfan of 0.005, 0.01 and 0.02 µg/L was derived for 99, 95 and 90 per cent of species respectively. However, because of endosulfan's potential to bioaccumulate ANZECC and ARMCANZ (2000) recommends that the 99 per cent protection figure of 0.005 µg/L for slightly-to-moderately disturbed systems be adopted.

Table 21: Marine data sets for endosulfan (Sunderam et al 2000)

| Species  | Geometric mean of Effects conc. $\mu\text{g/L}$ | Endpoint       | Toxicity measure |
|--|---|----------------|------------------|
| <b><i>Fish</i></b>                                       |   |                |                  |
| <i>Atherinops affinis</i> (topsmelt)                     | 1.3   | Mortality      | LC50, Acute      |
| <i>Cymatogaster aggregata</i> (shiner perch)             | 1.1   | Mortality      | LC50, Acute      |
| <i>Cyprinodon variegatus</i> (sheepshead minnow)         | 1.4   | Mortality      | LC50, Acute      |
| <i>Fundulus heteroclitus</i> (mummichog)                 | 1.2   | Mortality      | LC50, Acute      |
| <i>Lagodon rhomboides</i> (pinfish)                      | 0.3   | Mortality      | LC50, Acute      |
| <i>Leiostomus xanthurus</i> (spot)                       | 0.3   | Mortality      | LC50, Acute      |
| <i>Menidia beryllina</i> (inland silverside)             | 1.5   | Mortality      | LC50, Acute      |
| <i>Morone saxatilis</i> (striped bass)                   | 0.1   | Mortality      | LC50, Acute      |
| <i>Mugil cephalus</i> (striped mullet)                   | 1.5   | Mortality      | LC50, Acute      |
| <i>Mugil curema</i> (white mullet)                       | 0.6   | Mortality      | LC50, Acute      |
| <i>Oncorhynchus kisutch</i> (coho salmon, silver salmon) | 2.1   | Mortality      | LC50, Acute      |
| <b><i>Crustaceans</i></b>                                |   |                |                  |
| <i>Acartia tonsa</i> (calanoid copepod)                  | 0.1   | Mortality      | LC50, Acute      |
| <i>Callinectes sapidus</i> (blue crab)                   | 19  | Immobilisation | EC50, Acute      |
| <i>Callinectes sapidus</i>                               | 35  | Mortality      | LC50, Acute      |
| <i>Cancer magister</i> (Dungeness or edible crab)        | 15  | Immobilisation | EC50, Acute      |
| <i>Cancer magister</i>                                   | 15  | Mortality      | LC50, Acute      |
| <i>Crangon septemspinosa</i> (sand shrimp)               | 0.5   | Mortality      | LC50, Acute      |
| <i>Mysidopsis bahia</i> (opossum shrimp)                 | 1.0   | Mortality      | LC50, Acute      |
| <i>Palaemonetes pugio</i> (daggerblade grass shrimp)     | 0.7   | Mortality      | LC50, Acute      |
| <i>Penaeus aztecus</i> (brown shrimp)                    | 0.2   | Immobilisation | EC50, Acute      |
| <i>Penaeus aztecus</i>                                   | 0.4   | Mortality      | LC50, Acute      |
| <i>Penaeus duorarum</i> (pink shrimp (America))          | 0.04  | Mortality      | LC50, Acute      |
| <i>Penaeus indicus</i> (indian prawn)                    | 0.3   | Mortality      | LC50, Acute      |
| <i>Penaeus monodon</i> (jumbo tiger prawn)               | 17.8  | Mortality      | LC50, Acute      |
| <i>Scylla serrata</i> (crab)                             | 261   | Mortality      | LC50, Acute      |

| Species  | Geometric mean of Effects conc. µg/L | Endpoint     | Toxicity measure |
|--|--------------------------------------|--------------|------------------|
| <b><i>Molluscs</i></b>                                     |                                      |              |                  |
| <i>Crassostrea madrasensis</i> (oyster)                    | 17.4                                 | Mortality    | LC50, Acute      |
| <i>Crassostrea sp.</i> (oyster)                            | 65                                   | Growth       | EC50, Acute      |
| <i>Crassostrea virginica</i> (American or Virginia oyster) | 52                                   | Growth       | EC50, Acute      |
| <i>Katelysia opima</i> (marine bivalve)                    | 15.4                                 | Mortality    | LC50, Acute      |
| <i>Meretrix casta</i> (bivalve)                            | 16                                   | Mortality    | LC50, Acute      |
| <i>Paphia laterisulca</i> (estuarine clam)                 | 2.0                                  | Mortality    | LC50, Acute      |
| <b><i>Annelids</i></b>                                     |                                      |              |                  |
| <i>Dinophilus gyrotilatus</i> (archannelid)                | 1082                                 | Mortality    | LC50, Acute      |
| <i>Neanthes arenaceodentata</i> (polychaete)               | 197                                  | Mortality    | LC50, Acute      |
| <b><i>Echinoderms</i></b>                                  |                                      |              |                  |
| <i>Strongylocentrotus</i> (purple sea urchin)              | 230                                  | Mortality    | LC50, Chronic    |
| <b><i>Red algae</i></b>                                    |                                      |              |                  |
| <i>Champia parvula</i> (red algae)                         | 80                                   | Reproduction | NOEC, Chronic    |

#### Additional considerations

Additional data on endosulfan toxicity to corals has become available (Table 22).

Reductions in settlement and metamorphosis of greater than 50 per cent for the larvae of *A. millepora* were found for concentrations of 1.0 µg/L endosulfan (Markey et al 2007).

Table 22: Biological effects concentrations from direct toxicity testing of endosulfan.

| Species                    | Effect conc. µg/L | Endpoint                       | Toxicity measure | Reference         |
|----------------------------|-------------------|--------------------------------|------------------|-------------------|
| <b><i>Coral larvae</i></b> |                   |                                |                  |                   |
| <i>A. millepora</i>        | 1                 | ↓ settlement and metamorphosis | EC50 Acute, 18h  | Markey et al 2007 |

The minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups is met, so the BurrliOZ statistical distribution method (Campbell et al 2000) was used to derive a guideline trigger value for ecosystem protection. The additional EC50 effects concentration from Table 16 when entered into the BurrliOZ statistical distribution software (Campbell et al 2000) does not alter the existing ANZECC and ARMCANZ (2000) derived guideline value and consequently this trigger value is retained.

Recognising the potential to bioaccumulate, a **moderate reliability guideline trigger value of 0.005 µg/L** for endosulfan for protection of 99 per cent of species is recommended reef-wide.

#### 6.4.10 2-Methylethyl mercuric chloride (MEMC)

There are no data in the ANZECC and ARMCANZ (2000) water quality guideline database for toxicants (Sunderam et al 2000) for MEMC, however, data on MEMC toxicity to corals are available (Table 23). MEMC inhibited fertilisation and metamorphosis at 1 µg/L, with 50 per cent failure of fertilisation at 1.68 µg/L, and 50 per cent failure of metamorphosis at 2.5 µg/L (Markey et al 2007). Other effects including polyp retraction, tissue damage, expulsion of dinoflagellates, and reduced photosynthesis all occurred at concentrations of 10 µg/L (Markey et al 2007).

Table 23: Biological effects concentrations from direct toxicity testing of MEMC

| Species                    | Effects conc.<br>µg/L | Endpoint   | Toxicity measure | Reference         |
|----------------------------|-----------------------|--|------------------|-------------------|
| <b><i>Coral</i></b>        |                       |  |                  |                   |
| <b><i>Coral larvae</i></b> |                       |  |                  |                   |
| <i>A. millepora</i>        | 1                     | ↓fertilisation and metamorphosis                                 | LOEC             | Markey et al 2007 |
| <i>A. millepora</i>        | 2.5                   | ↓metamorphosis   | EC50, Acute, 18h | Markey et al 2007 |
| <i>A. millepora</i>        | 1.68                  | ↓ fertilisation  | EC50 Acute, 3h   | Markey et al 2007 |
| <i>A. millepora</i>        | 10                    | Polyp retraction, tissue damage, loss of algae, ↓ photosynthesis | LOEC Acute, 96h  | Markey et al 2007 |

The minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups is not met, so the BurriOZ statistical distribution method cannot be applied.

Since there are data on only one taxonomic group an assessment factor of 1000 was applied to the effects concentration to convert the EC50 acute effect to a chronic NOEC for the guideline trigger value (Warne 2001). This results in a value of 0.002µg/L for MEMC.

**A low reliability guideline trigger value of 0.002 µg/L was derived for MEMC.**

#### 6.4.11 Diazinon

The ANZECC and ARMCANZ water quality guideline database for toxicants (Sunderam et al 2000) has two marine data sets reported for diazinon (Table 24). Because of the limited data set the moderate reliability freshwater guideline concentration was applied with a low reliability. These are 0.00003, 0.01 and 0.2 µg/L respectively, for protection of 99, 95 and 90 per cent of species.

Table 24: Marine data sets for diazinon (Sunderam et al 2000)

| Species                                     | Effects conc.<br>µg/L | Endpoint  | Toxicity measure |
|---|-----------------------|-----------|------------------|
| <b><i>Crustaceans</i></b>                   |                       |           |                  |
| <i>Mysidopsis bahia</i><br>(opossum shrimp) | 6.0                   | Mortality | LC50, Acute, 96h |
| <i>Penaeus duorarum</i><br>(pink shrimp)    | 21                    | Mortality | LC50, Acute, 96h |



Additional data on diazinon toxicity to sea urchins are available (Table 25). Reduction in fertilisation in urchin eggs of *Paracentrotus lividus* occurs at 30 000µg/L of diazinon (Pesando et al 2003) while molecular activity such as lectin binding and acetylcholinesterase (neuromuscular function) inhibition occurring at 30 µg/L.

Table 25: Biological effects concentrations from direct toxicity testing of diazinon

| Species            | Effect conc.<br>µg/L | Endpoint                           | Toxicity<br>measure  | Reference          |
|--------------------|----------------------|------------------------------------|----------------------|--------------------|
| <i>Echinoderms</i> |                      |                                    |                      |                    |
| <i>Urchin eggs</i> |                      |                                    |                      |                    |
| <i>P. lividus</i>  | 30 000               | ↓ fertilisation                    | LOEC                 | Pesando et al 2003 |
| <i>P. lividus</i>  | 30                   | ↓ neuromuscular<br>system function | Not coded<br>Chronic | Pesando et al 2003 |

The minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups is not met, so the BurrliOZ statistical distribution method to derive a guideline trigger value cannot be applied.

Combining the ANZECC and ARMCANZ water quality guideline database for toxicants (Sunderam et al 2000) with the effects concentration from Table 25, provides at least three acute EC50, IC50, or LC50 values (if we assume Pesando's non-coded toxicity measure was an LC50 or EC50 value). However, biochemical endpoints such as inhibition of acetylcholinesterase activity are not considered valid to use in the ANZECC and ARMCANZ (2000) guidelines, so this data was not used in derivation.

Since there are data on only limited taxonomic groups, an assessment factor of 1000 was applied to the lowest of the effects concentration to convert the LC50 acute effect to a chronic NOEC for the guideline trigger value (Warne 2001). This results in a low reliability guideline trigger value of 0.006 µg/L for diazinon, which is between the 99<sup>th</sup> and 95<sup>th</sup> percentile freshwater guideline adopted by ANZECC and ARMCANZ (2000).

At this stage, the Great Barrier Reef Marine Park Authority adopts the ANZECC and ARMCANZ (2000) guideline, applying the moderate reliability freshwater guideline with a low reliability.

**A low reliability guideline trigger value of 0.00003, 0.01 and 0.2 µg/L is applied for diazinon for protection of 99, 95 and 90 per cent of marine species, respectively.**

#### 6.4.12 Pesticide summary

For high ecological value water bodies, a guideline concentration that is protective of 99 per cent of species is ideal. In section 1.3, the environmental values of the Great Barrier Reef Marine Park were discussed. Regardless of the current condition of the waters aquatic ecosystem protection is the environmental value currently applied to the entire World Heritage Area. Even in the highly disturbed trawl grounds any effects of pesticides and biocides would be considered unacceptable. Therefore, trigger values for these parameters as derived in these guidelines apply to all of the five water bodies at the concentration protective of 99 per cent of species.

Sufficient data exists to derive moderate reliability trigger value concentrations for ecosystem protection for diuron, atrazine, ametryn, endosulfan and 2,4-D. Chlorpyrifos was the only pesticide that met high reliability trigger value data requirements. These guidelines adopt the high reliability trigger value from the ANZECC and ARMCANZ (2000) guideline for chlorpyrifos. These values are summarised in Table 26.

Table 26: Summary of high and moderate reliability guideline trigger values for pesticides

| <b>Pesticide</b> | <b>99% species protection</b>                   | <b>95% species protection</b> |
|------------------|---|-------------------------------|
|                  | <b>High reliability trigger value, µg/L</b>     |                               |
| Chlorpyrifos     | 0.0005  | 0.009                         |
|                  | <b>Moderate reliability trigger value, µg/L</b> |                               |
| Diuron           | 0.9   | 1.6                           |
| Atrazine         | 0.6   | 1.4                           |
| Ametryn          | 0.5   | 1.0                           |
| 2,4-D            | 0.8   | 30.8                          |
| Endosulfan       | 0.005   | 0.005 <sup>a</sup>            |

<sup>a</sup> 99<sup>th</sup> percentile value recommended reef-wide because of bioaccumulation

Where the minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups is not met a low reliability guideline can be derived in a number of ways. Except for MEMC and hexazinone these guidelines adopt the ANZECC and ARMCANZ (2000) method of using a freshwater guideline with lower reliability.

There was sufficient EC50 or LC50 data available for hexazinone to apply the division of the lowest of the acute values by 100 (OECD 1992) to provide a low reliability guideline trigger value.

ANZECC and ARMCANZ (2000) did not include an assessment of MEMC. Data have since become available on the toxicity of this fungicide. Since there are data on only one taxonomic group an assessment factor of 1000 was applied to the effect concentration to convert an acute effect to a chronic for the guideline trigger value. These values are presented here in Table 27.

Table 27: Summary of low reliability guideline trigger values for pesticides

| <b>Pesticide</b> | <b>Low reliability guideline trigger value, µg/L</b> |
|------------------|--|
| Simazine         | 0.2  |
| Hexazinone       | 1.2  |
| Tebuthiuron      | 0.02   |
| MEMC             | 0.002  |
| Diazinon         | 0.00003  |

In accordance with ANZECC and ARMCANZ (2000) guidelines, low reliability trigger values are only to be used as indicative working levels for interim guidance. Monitoring programs should ascertain and report on the concentration of these contaminants in Great Barrier Reef waters. The management actions that result from exceedance may be to improve management practices to further minimise loss from adjacent catchments, or to search, or test, for more data of sufficient quality to further assess the likely risk to aquatic ecosystems associated with further exposure to these contaminants.

## 6.5 Tributyltin

The ANZECC and ARMCANZ water quality guideline database for toxicants (Sunderam et al 2000) reports seventeen marine data sets for tributyltin that were used (Table 28). The ANZECC and ARMCANZ (2000) guidelines derive high reliability trigger values for marine water for tributyltin of 0.0004, 0.006 and 0.02 µg/L respectively for protection of 99, 95 and 90 per cent of species.

Table 28: Marine data for tributyltin (Sunderam et al 2000)

| Species   | Effects conc.<br>µg/L | Endpoint  | Toxicity measure     |
|---|-----------------------|-----------|----------------------|
| <b><i>Fish</i></b>  |                       |           |                      |
| <i>Cyprinodon variegatus</i><br>(sheepshead minnow)           | 0.6                   | Mortality | NOEC, Chronic, 720h  |
| <b><i>Crustaceans</i></b>                                     |                       |           |                      |
| <i>Acartia tonsa</i><br>(calanoid copepod)                    | 0.0044                | Mortality | NOEC, Chronic, 144h  |
| <i>Acartia tonsa</i>  | 0.0042                | Mortality | NOEC, Chronic, 144h  |
| <b><i>Molluscs</i></b>  |                       |           |                      |
| <i>Crassostrea virginica</i><br>(American or Virginia oyster) | 0.13                  | Growth    | NOEC, Chronic, 1584h |
| <i>Mytilus edulis</i><br>(common bay mussel, blue)            | 0.8                   | Growth    | NOEC, Chronic, 792h  |
| <i>Mytilus edulis</i>   | 0.002                 | Growth    | NOEC, Chronic, 792h  |
| <i>Mytilus edulis</i>   | 0.05                  | Growth    | NOEC, Chronic, 1584h |
| <i>Scrobicularia plana</i><br>(bivalve)                       | 1                     | Mortality | NOEC, Chronic, 522h  |
| <i>Scrobicularia plana</i>                                    | 1                     | Mortality | NOEC, Chronic, 720h  |
| <i>Scrobicularia plana</i>                                    | 0.05                  | Mortality | NOEC, Chronic, 720h  |
| <b><i>Diatom</i></b>  |                       |           |                      |
| <i>Skeletonema costatum</i>                                   | 0.14                  | Growth    | EC50, Chronic, 72h   |
| <i>Skeletonema costatum</i>                                   | 376.5                 | Growth    | EC50, Chronic, 72h   |
| <i>Skeletonema costatum</i>                                   | 0.13                  | Growth    | EC50, Chronic, 72h   |
| <i>Skeletonema costatum</i>                                   | 0.13                  | Growth    | EC50, Chronic, 72h   |
| <i>Skeletonema costatum</i>                                   | 5.1                   | Growth    | EC50, Chronic, 96h   |
| <i>Thalassiosira pseudonana</i>                               | 0.48                  | Growth    | EC50, Chronic, 72h   |
| <i>Thalassiosira pseudonana</i>                               | 0.41                  | Growth    | EC50, Chronic, 72h   |

There is also additional data cited in section 8.3 including two additional fish species, four crustaceans, and one algae.

### Additional considerations

Additional data on tributyltin toxicity to corals has become available since ANZECC and ARMCANZ (2000) was published (Table 29). Tributyltin inhibited larval metamorphosis of *A. millepora* at an IC50 of 2 µg/L (Negri and Heyward 2001), while fertilisation was inhibited (IC50) at 200 µg/L (Negri and Heyward 2001).

Table 29 Biological effects concentrations from direct toxicity testing of tributyltin

|                     | Effects conc.<br>µg/L | Endpoint        | Toxicity<br>measure | Reference              |
|---------------------|-----------------------|-----------------|---------------------|------------------------|
| <i>Coral</i>        |                       |                 |                     |                        |
| <i>Coral larvae</i> |                       |                 |                     |                        |
| <i>A. millepora</i> | 200                   | ↓ fertilisation | IC50, Acute, 4h     | Negri and Heyward 2001 |
| <i>A. millepora</i> | 2                     | ↓ metamorphosis | IC50, Acute, 24h    | Negri and Heyward 2001 |

As the new data is for the same species but two different endpoints, the lower of the effects concentration is used to derive the trigger value. An assessment factor of 16.26 was applied for conversion of the acute IC50 data to chronic NOEC. Addition of this data into the BurriOZ statistical distribution software (Campbell et al 2000) run did not alter the trigger value derived. Therefore, the Great Barrier Reef Marine Park Authority adopts the high reliability trigger value aligning with the ANZECC and ARMCANZ (2000) guideline.

Most large scale dredging and spoil disposal within the Great Barrier Reef Marine Park is associated with ports. The work is undertaken to maintain port accessibility which is important to the regional economy. Proposals for spoil disposal in the Great Barrier Reef Marine Park will continue to be assessed in accordance with the Great Barrier Reef Marine Park Authority's policies for Environmental Impact Management, Dredging and Spoil Disposal, and Risk Management.

There are existing approved dumping grounds for spoil within the Great Barrier Reef Marine Park. Many of these grounds have been used repeatedly for a number of years. These sites are carefully managed to ensure any adverse effects are prevented or minimised. In recognition of their slightly to moderately disturbed state the Great Barrier Reef Marine Park Authority assign a guideline trigger level protective of 95 per cent of species. In the case of tributyltin that results in the 0.006 µg/L guideline trigger value being applied.

In the event of any future proposal for new spoil disposal sites determination of the appropriate level of protection will be one of the considerations at the time of assessment. Such an assessment would include, but not be limited to an assessment of the conservation values of the area likely to be affected by disposal activities. The Great Barrier Reef Marine Park Authority has an open and transparent decision making process and works with stakeholders to achieve successful management and mitigation of environmental impacts associated with spoil disposal.

**High reliability guideline trigger values of 0.0004, 0.006 and 0.02 µg/L are applied for tributyltin for protection of 99, 95 and 90 per cent of species respectively.**

## 6.6 Sublethal effects consideration

Sublethal effects have not been included in derivations of guideline trigger values. However, minimisation of these impacts could prove critical to long term protection of the ecosystem. The effects data is presented here as an information source to facilitate further discussion, along with the change in the trigger value if the data are included in the derivation.

### 6.6.1 Diuron

There are numerous additional reports (Table 30) in the open scientific literature that have become available since ANZECC and ARMCANZ (2000) was published. Reports on diuron toxicity to corals (Jones and Kerswell 2003, Jones et al 2003, Owen et al 2003, Råberg et al 2003, Jones 2004, Negri et al 2005), seagrass (Haynes et al 2000b, Ralph 2000, Macinnis-Ng and Ralph 2003, Chesworth et al 2004), phytoplankton (Magnusson et al 2006, Seery et al 2006) and mangroves (Duke et al 2003, Duke and Bell 2005) are presented here.

The results show that exposure of a number of organisms to diuron reduces the efficiency of photosynthesis. However, as discussed in the pesticide introduction section, photosynthesis responses are not universally accepted as an appropriate endpoint for deriving toxicity guidelines. This response could well be an indicator of sublethal ecosystem impacts, and while it may not, on its own, lead to mortality creates a concern as to the potential detrimental additive effects of photosynthesis suppression on marine organisms. Furthermore these effects might be reasonably expected to occur on the primary production end of the ecosystem with consequent cascading impacts to all higher levels of the ecosystem.

In the corals *Acropora formosa*, *Montipora digitata*, *Porites cylindrica* and *Seriatopora hystrix* suppression of photosynthesis occurred at a concentration of 1 µg/L diuron after ten hours exposure (Jones et al 2003). During a four-day exposure *M. digitata* showed suppression of photosynthesis occurred at a concentration of 1 µg/L diuron and visible bleaching occurred at a concentration of 10 µg/L (Jones et al 2003).

Further research at varying light levels confirmed photosynthesis suppression occurred at exposures of 1 µg/L, and higher in the coral *S. hystrix* (Jones 2004). Two different light levels were tested with these concentrations, (50 per cent and five per cent surface irradiation), and photosynthesis suppression was found to be less intense at reduced light levels. Bleaching occurred in the corals exposed to 10 µg/L and higher concentrations, although at the higher concentration bleaching only occurred at the higher of the two light levels (Jones 2004).

Lowest observable effects occurred at concentrations of 0.3 µg/L diuron in symbionts of the coral *S. hystrix*, within host tissue (Jones and Kerswell 2003) and an EC50 of 2.3 µg/L. Lowest observable effects occurred at concentrations of 0.3 µg/L diuron in symbionts of the coral *A. formosa*, within host tissue (Jones and Kerswell 2003) and an EC50 of 2.7 µg/L.

Isolated symbiotic dinoflagellates of *Stylophora pistillata* showed suppression of photosynthesis at exposures as low as 0.25 µg/L of diuron (Jones et al 2003). Using <sup>14</sup>C uptake studies, lowest observable effects on photosynthesis occurred at concentrations of 2 µg/L diuron in isolated zooxanthellae of the corals *Diploria strigosa*, *Madracis mirabilis* and *Favia fragum* after six hours (Owen et al 2003). This reduction was also evident in *M. mirabilis* at concentrations of 1 µg/L diuron after eight hours exposure (Owen et al 2003).

*Pocillopora damicornis* (recruits and adults) bleached at 10 µg/L concentration (Negri et al 2005). *P. damicornis* (recruits and adults) and *Acropora millepora* (adults) also showed reduced photosynthetic efficiency at 1 µg/L diuron, with apparent full recovery after 14 days at no exposure (Negri et al 2005).

There was no significant inhibition of fertilisation or metamorphosis in *A. millepora*, *Montipora aequituberculata* or *P. damicornis* at concentrations of diuron well over 30 µg/L (Negri et al 2005). *A. millepora* showed significant metamorphosis inhibition at 300 µg/L (Negri et al 2005).

Significant reduction in gross primary production rate, and gross primary production to respiration ratio in the hermatypic coral *P. cylindrica* occurred at 10 µg/L concentration of diuron (Råberg et al 2003).

Diuron suppresses photosynthesis in the seagrasses *Cymodocea serrulate*, *Zostera capricorni* and, *Halophila ovalis* at concentrations in seawater of 10 µg/L, 0.1 µg/L and 0.1 µg/L respectively, and no full recovery occurred after five further days of no applied diuron exposure (Ralph 2000, Haynes et al 2000b). Diuron suppressed photosynthesis in the seagrass *Z. capricorni* at concentrations in seawater of 10 µg/L, with recovery after four days (Macinnis-Ng and Ralph 2003). Reductions in photosynthetic yield of *Zostera marina* occur at concentrations of 1.0 µg/L, while reduced growth occurred at 5.0 µg/L (Chesworth et al 2004).

In field observations, herbicide levels in Johnstone and Daintree River mangrove sediments correlated with upstream distributions of *A. marina*, noting this species was absent where diuron concentrations exceeded 2 µg diuron/kg of sediment. Dieback was observed near Mackay where diuron concentrations in sediments were in the range 6-8 µg/kg (Duke et al 2003, Bell and Duke 2005). The findings have been translated to a threshold concentration of 2 µg diuron/kg of sediment as the level above which dieback of the mangrove species *A. marina* may be expected.

Marine diatoms sensitivities to diuron estimated IC10 concentrations in the range of 0.1-0.19 µg/L for *Nitzschia closterium*, *Phaeodactylum tricornutum* and *Dunaliella tertiolecta* after less than 20 minutes exposure (Bengston Nash et al 2005a). The lowest observable effects concentration was 0.05 µg/L (Bengston Nash et al 2005b). *P. tricornutum* also showed significant inhibition of photosynthetic yield (IC50) at 3.3 µg/L diuron (Schreiber et al 2002). Several species of estuarine benthic diatoms (*Navicula* sp) showed significant inhibition of photosynthetic yield at 2.9 µg/L diuron (Magnusson et al 2006).

Diuron inhibits photosynthesis of the crustose coralline algae *Porolithon onkodes* at concentrations of 2.9 µg/L (Harrington et al 2005). This may also compromise coral recruitment, as crustose coralline algae are a critical settlement inducer for many coral species (Heyward and Negri 1999).

Gametes from the macro algae *Hormosira banksii* showed significant inhibition of photosynthesis (EC50 measured by effective quantum yield of photosystem II) at concentrations of 1.65 µg/L diuron (Seery et al 2006).

Table 30: Biological effects concentrations from direct toxicity testing of diuron

| Species              | Effects conc.<br>µg/L | Endpoint         | Toxicity<br>measure | Reference                  |
|----------------------|-----------------------|------------------|---------------------|----------------------------|
| <b>Seagrass</b>      |                       |                  |                     |                            |
| <i>C. serrulata</i>  | 10                    | ↓ photosynthesis | LOEC                | Haynes et al 2000b         |
| <i>Z. capricorni</i> | 10                    | ↓ photosynthesis | LOEC                | Macinnis-Ng and Ralph 2003 |
| <i>Z. capricorni</i> | 5.0                   | ↓ growth         | LOEC                | Chesworth et al 2004       |
| <i>Z. capricorni</i> | 1.0                   | ↓ photosynthesis | LOEC                | Chesworth et al 2004       |
| <i>H. ovalis</i>     | 0.1                   | ↓ photosynthesis | LOEC                | Haynes et al 2000b         |
| <i>Z. capricorni</i> | 0.1                   | ↓ photosynthesis | LOEC                | Haynes et al 2000b         |

| Species                           | Effects conc.<br>µg/L | Endpoint   | Toxicity<br>measure | Reference                       |
|-----------------------------------|-----------------------|--|---------------------|---------------------------------|
| <b>Corals</b>                     |                       |  |                     |                                 |
| <b>Isolated<br/>zooxanthellae</b> |                       |  |                     |                                 |
| <i>D. strigosa</i>                | 2                     | ↓ <sup>14</sup> C incorporation  | LOEC                | Owen et al 2003                 |
| <i>F. fragum</i>                  | 2                     | ↓ <sup>14</sup> C incorporation  | LOEC                | Owen et al 2003                 |
| <i>M. mirabilis</i>               | 1                     | ↓ <sup>14</sup> C incorporation  | LOEC                | Owen et al 2003                 |
| <i>S. pistillata</i>              | 0.25                  | ↓ photosynthesis   | LOEC                | Jones et al 2003                |
| <b>Larvae</b>                     |                       |  |                     |                                 |
| <i>A. millepora</i>               | 300                   | ↓ Metamorphosis  | LOEC                | Negri et al 2005                |
| Coral recruits                    |                       |  |                     |                                 |
| <i>P. damicornis</i>              | 10                    | Loss of algae  | LOEC                | Negri et al 2005                |
| <i>P. damicornis</i>              | 1                     | ↓ photosynthesis   | LOEC                | Negri et al 2005                |
| <b>Adult colonies</b>             |                       |  |                     |                                 |
| <i>M. digitata</i>                | 10                    | Loss of algae  | LOEC                | Jones et al 2003                |
| <i>P. damicornis</i>              | 10                    | Loss of algae  | LOEC                | Negri et al 2005                |
| <i>S. hystrix</i>                 | 10                    | Loss of algae  | LOEC                | Jones 2004                      |
| <i>P. cylindrica</i>              | 10                    | GPP* rate, GPP to<br>respiration ration,<br>effective quantum<br>yield | LOEC                | Råberg et al 2003               |
| <i>A. formosa</i>                 | 1                     | ↓ photosynthesis   | LOEC                | Jones et al 2003                |
| <i>P. cylindrica</i>              | 1                     | ↓ photosynthesis   | LOEC                | Jones et al 2003                |
| <i>M. digitata</i>                | 1                     | ↓ photosynthesis   | LOEC                | Jones et al 2003                |
| <i>S. hystrix</i>                 | 1                     | ↓ photosynthesis   | LOEC                | Jones et al 2003, Jones<br>2004 |
| <i>A. millepora</i>               | 1                     | ↓ photosynthesis   | LOEC                | Negri et al 2005                |
| <i>P. damicornis</i>              | 1                     | ↓ photosynthesis   | LOEC                | Negri et al 2005                |
| <i>A. formosa</i>                 | 0.3                   | ↓ photosynthesis   | LOEC                | Jones and Kerswell 2003         |
| <i>A. formosa</i>                 | 2.7                   | ↓ photosynthesis   | EC50                | Jones and Kerswell 2003         |
| <i>S. hystrix</i>                 | 0.3                   | ↓ photosynthesis   | LOEC                | Jones et al 2003                |
| <i>S. hystrix</i>                 | 2.3                   | ↓ photosynthesis   | EC50                | Jones et al 2003                |
| <i>S. hystrix</i>                 | 0.3                   | ↓ photosynthesis   | LOEC                | Jones and Kerswell 2003         |
| <b>Macro algae</b>                |                       |  |                     |                                 |
| <i>H. banksii</i>                 | 1.65                  | ↓ photosynthesis   | EC50                | Seery et al 2006                |
| <b>Red algae</b>                  |                       |  |                     |                                 |
| <i>P. onkodes</i>                 | 2.9                   | ↓ photosynthesis   | LOEC                | Harrington et al 2005           |
| <b>Diatoms</b>                    |                       |  |                     |                                 |
| <i>P. tricornutum</i>             | 3.3                   | ↓ photosynthesis   | I50                 | Schreiber et al 2002            |
| <i>Navicula sp</i>                | 2.9                   | ↓ photosynthesis   | IC50<br>Acute, 6 m  | Magnusson et al 2006            |
| <i>D. tertiolecta</i>             | 0.05                  | ↓ photosynthesis   | LOEC                | Bengston Nash et al 2005a       |
| <i>N. closterium</i>              | 0.1-0.19              | Sensitivity  | IC10                | Bengston Nash et al 2005a       |
| <i>N. closterium</i>              | 0.05                  | Sensitivity  | LOEC                | Bengston Nash et al 2005a       |
| <i>P. tricornutum</i>             | 0.1-0.19              | Sensitivity  | IC10                | Bengston Nash et al 2005a       |
| <i>D. tertiolecta</i>             | 0.11                  | ↓ photosynthesis   | IC10                | Bengston Nash et al 2005a       |

| Species          | Effects conc.<br>µg/L | Endpoint         | Toxicity<br>measure | Reference                           |
|------------------|-----------------------|------------------|---------------------|-------------------------------------|
| <b>Mangrove</b>  |                       |                  |                     |                                     |
| <i>A. marina</i> | 1.1                   | Health           | NOEC                | Duke et al 2003, 2005               |
| <i>A. marina</i> | 1.5<x≤2               | Reduced health   | LOEC                | Duke et al 2003, Bell and Duke 2005 |
| <i>A. marina</i> | >2.0                  | Dieback/ absence | Mortality           | Duke et al 2003, Bell and Duke 2005 |

\* Gross Primary Production

These studies report LC50, IC50, EC50, IC10, LOEC and NOEC toxicity measures. Most of the acute studies have the tests lasting for less than a day. Where more than one toxicity value was reported for the same endpoint in the same species the geometric mean of the values was entered (Van de Plassche et al 1995). An assessment factor of 10 was applied to convert acute LC or EC50s to chronic NOECs, and a factor of 2.5 to convert acute LOECs to chronic NOECs. LC or EC50s were used in preference to LOECs. IC10, and NOEC toxicity measures were not used at all.

Including these responses with the other effects data presented in section 6.4.1 for diuron in the BurrliOZ statistical distribution software (Campbell et al 2000) run, results in the derivation of moderate reliability guideline trigger values of 0.01, 0.06 and 0.1 µg/L for diuron for protection of 99, 95 and 90 per cent of species respectively.

At this stage, with implementation of numerous management actions underway, the Great Barrier Reef Marine Park Authority sets the trigger value without the sublethal responses included ie 0.9 µg/L and 1.6 µg/L for diuron for protection of 99, and 95 per cent of species respectively.

Additional consideration of the potential sublethal ecosystem effects of suppressed photosynthesis is recommended.

## 6.6.2 Atrazine

Sublethal effects data on atrazine toxicity to marine species are shown in Table 31. There are numerous studies that have become available since ANZECC and ARMCANZ (2000) was published. Reports on toxicity to corals (Jones and Kerswell 2003, Jones et al 2003, Owen et al 2003), seagrass (Ralph 2000; Macinnis-Ng and Ralph 2003; Schwarzschild et al 1994) mangroves (Duke et al 2005) and micro flora (Magnusson 2006) are presented here.

In the corals *A. formosa*, *M. digitata*, and *P. cylindrica* a suppression of photosynthesis occurred at an exposure of 3 µg/L atrazine for 10 hours, with apparent full recovery after the same period in the absence of atrazine (Jones et al 2003). The 10-hour EC50 values for four coral species range from 37-88 µg/L (Jones and Kerswell 2003, Jones et al 2003). Lowest observable effects occurred at concentrations of 3 µg/L and an EC50 of 45 µg/L atrazine in symbionts of the coral *S. hystrix*, within host tissue (Jones and Kerswell 2003).

Using <sup>14</sup>C uptake studies, lowest observable effects on photosynthesis occurred at concentrations of 100 µg/L atrazine in isolated zooxanthellae of the coral *D. strigosa*, *M. mirabilis* and *F. fragum* (Owen et al 2003).

Atrazine suppresses photosynthesis in the seagrass *H. ovalis*, *Z. capricorni* at concentrations of 10 µg/L in seawater (Ralph 2000; Macinnis-Ng and Ralph 2003). These studies confirmed the findings of Schwarzschild et al (1994) as cited in Macinnis-Ng and Ralph (2003).



Several species of estuarine benthic diatoms (*Navicula sp*) showed significant inhibition of photosynthetic yield at 47 µg/L atrazine (Magnusson et al 2006).

Table 31: Biological effects concentrations from direct toxicity testing of atrazine

| Species                        | Effect conc. µg/L | Endpoint                        | Toxicity measure      | Reference                  |
|--------------------------------|-------------------|---------------------------------|-----------------------|----------------------------|
| <b>Seagrass</b>                |                   |                                 |                       |                            |
| <i>H. ovalis</i>               | 10                | ↓ photosynthesis                | LOEC                  | Ralph 2000                 |
| <i>Z. capricorni</i>           | 10                | ↓ photosynthesis                | LOEC                  | Macinnis-Ng and Ralph 2003 |
| <b>Corals</b>                  |                   |                                 |                       |                            |
| <i>D. strigosa</i>             | 100               | ↓ <sup>14</sup> C incorporation | LOEC                  | Owen et al 2003            |
| <i>M. mirabilis</i>            | 100               | ↓ <sup>14</sup> C incorporation | LOEC                  | Owen et al 2003            |
| <i>F. fragum</i>               | 100               | ↓ <sup>14</sup> C incorporation | LOEC                  | Owen et al 2003            |
| <b>Adult colonies</b>          |                   |                                 |                       |                            |
| <i>A. formosa</i>              | 3                 | ↓ photosynthesis                | LOEC                  | Jones et al 2003           |
| <i>P. cylindrica</i>           | 3                 | ↓ photosynthesis                | LOEC                  | Jones et al 2003           |
| <i>M. digitata</i>             | 3                 | ↓ photosynthesis                | LOEC                  | Jones et al 2003           |
| <i>S. hystrix</i>              | 3                 | ↓ photosynthesis                | LOEC                  | Jones and Kerswell 2003    |
| <i>S. hystrix</i>              | 45                | ↓ photosynthesis                | EC50                  | Jones and Kerswell 2003    |
| <b>Macrophyte</b>              |                   |                                 |                       |                            |
| <i>Potamogeton perfoliatus</i> | 80                | ↓ photosynthesis                | IC50                  | NRA 1997                   |
| <b>Diatoms</b>                 |                   |                                 |                       |                            |
| <i>Navicula sp</i>             | 47                | ↓ photosynthesis                | IC50, Acute, 6 minute | Magnusson et al 2006       |

These studies report IC50, EC50, and LOEC toxicity measures. Most of the acute studies have the tests lasting for less than a day. An assessment factor of 20.21 was applied to convert acute LC or EC50s to chronic NOECs, and a factor of 2.5 to convert acute LOECs to chronic NOECs. LC or EC50s toxicity measures were used in preference to LOECs.

Including these responses in the BurrliOZ statistical distribution software (Campbell et al 2000) run, with the atrazine data in section 6.4.2, resulted in moderate reliability guideline trigger values of 0.5, 1.1 and 1.8 µg/L for atrazine for protection of 99, 95 and 90 per cent of species respectively.

At this stage, with implementation of numerous management actions underway, the Great Barrier Reef Marine Park Authority sets the trigger value without the sublethal responses included ie 0.6 µg/L and 1.4 µg/L for atrazine for protection of 99 and 95 per cent of species respectively.

Additional consideration of the potential sublethal ecosystem effects of suppressed photosynthesis is recommended.

### 6.6.3 Ametryn

Sublethal data on ametryn toxicity to corals (Jones and Kerswell 2003) has become available since ANZECC and ARMCANZ (2000) was published (Table 32).

Symbiotic dinoflagellates showed significant inhibition (EC50) of photosynthesis at ametryn concentrations of 1.7 µg/L (Jones and Kerswell 2003). Lowest observable effects occurred at concentrations of 0.3 µg/L in symbionts of the coral *S. hystrix* within host tissue (Jones and Kerswell 2003).

Table 32: Biological effects concentrations from direct toxicity testing for ametryn

| Species               | Effect conc.<br>µg/L | Endpoint         | Toxicity<br>measure | Reference               |
|-----------------------|----------------------|------------------|---------------------|-------------------------|
| <b>Corals</b>         |                      |                  |                     |                         |
| <b>Adult colonies</b> |                      |                  |                     |                         |
| <i>S. hystrix</i>     | 0.3                  | ↓ photosynthesis | LOEC                | Jones and Kerswell 2003 |
| <i>S. hystrix</i>     | 1.7                  | ↓ photosynthesis | EC50                | Jones and Kerswell 2003 |

An assessment factor of 10 was applied to convert the acute EC50 to a chronic NOEC in preference to the LOEC toxicity measure.

Including this response with the data in the BurrliOZ statistical distribution software (Campbell et al 2000) run at section 6.4.3, results in the derivation of moderate reliability guideline trigger values of 0.2, 0.4 and 0.7 µg/L for ametryn for protection of 99, 95 and 90 per cent of species respectively.

At this stage, with implementation of numerous management actions underway, the Great Barrier Reef Marine Park Authority sets the trigger value without the sublethal response included ie 0.5 µg/L and 1.0 µg/L for ametryn for protection of 99 and 95 per cent of species respectively.

Additional consideration of the potential sublethal ecosystem effects of suppressed photosynthesis is recommended.

#### 6.6.4 Simazine

Sublethal effects data has become available since ANZECC and ARMCANZ (2000) was published including effects of simazine toxicity to corals (Jones and Kerswell 2003, Owen et al 2003) and micro flora (Magnusson et al 2006) (Table 33).

Lowest observable effects occurred at concentrations of 30 µg/L simazine in symbionts of the coral *S. hystrix*, within host tissue (Jones and Kerswell 2003) and an EC50 of 150 µg/L.

Using <sup>14</sup>C uptake studies, lowest observable effects on photosynthesis occurred at concentrations of 100 µg/L simazine in isolated zooxanthellae of the coral *D. strigosa*, *M. mirabilis* and *F. fragum* (Owen et al 2003).

Several species of estuarine benthic diatoms (*Navicula sp*) showed significant inhibition of photosynthetic yield at 110 µg/L simazine (Magnusson et al 2006).

Table 33: Biological effects concentrations from direct toxicity testing of simazine

| Species  | Effects conc. $\mu\text{g/L}$ | Endpoint                                   | Toxicity measure      | Reference               |
|--|-------------------------------|--|-----------------------|-------------------------|
| <b>Corals</b><br><i>Isolated zooxanthellae</i> |                               |  |                       |                         |
| <i>D. strigosa</i>                             | 100                           | $\downarrow$ $^{14}\text{C}$ incorporation | LOEC                  | Owen et al 2003         |
| <i>M. mirabilis</i>                            | 100                           | $\downarrow$ $^{14}\text{C}$ incorporation | LOEC                  | Owen et al 2003         |
| <i>F. fragum</i>                               | 100                           | $\downarrow$ $^{14}\text{C}$ incorporation | LOEC                  | Owen et al 2003         |
| <b>Corals</b><br><i>Adult colonies</i>         |                               |  |                       |                         |
| <i>S. hystrix</i>                              | 30                            | $\downarrow$ photosynthesis                | LOEC                  | Jones and Kerswell 2003 |
| <i>S. hystrix</i>                              | 150                           | $\downarrow$ photosynthesis                | EC50                  | Jones and Kerswell 2003 |
| <b>Microphyto- benthos</b>                     |                               |  |                       |                         |
| <i>Navicula sp</i>                             | 110                           | $\downarrow$ photosynthesis                | IC50, Acute, 6 minute | Magnusson et al 2006    |

Including these data with those in section 6.4.4 does result in sufficient data to meet the minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups, so the BurrliOZ statistical distribution method to derive a guideline trigger value can be applied. However, as we have discussed, reduced photosynthesis endpoints are not used in derivation of guidelines and the software does warn that the number of data are small and that results should be interpreted with caution.

Out of interest in its comparison to the freshwater guideline value the BurrliOZ statistical distribution software (Campbell et al 2000) was run. The same assessment factors were used as in section 6.4.4. The NOECs were used for the sea bream. An assessment factor of 10 was applied to convert acute EC50 to a chronic NOEC in preference to using the LOEC toxicity measure. An assessment factor of five was applied to convert a chronic EC50 to a chronic NOEC. The run results in trigger values of 4.3 and 10.4  $\mu\text{g/L}$  for simazine for protection of 99 and 95 per cent of species respectively. These results are similar to the 95th and 90th percentile freshwater guideline (3.2  $\mu\text{g/L}$  and 11  $\mu\text{g/L}$  respectively), hence an order of magnitude greater than the ANZECC and ARMCANZ adopted freshwater guideline.

At this stage, with implementation of numerous management actions underway, the Great Barrier Reef Marine Park Authority sets the trigger value without the sublethal response included ie 0.2  $\mu\text{g/L}$  and 3.2  $\mu\text{g/L}$  for simazine for protection of 99 and 95 per cent of species respectively.

Additional consideration of the potential sublethal ecosystem effects of suppressed photosynthesis is recommended.

### 6.6.5 Hexazinone

Sublethal effect data on hexazinone toxicity to corals has become available since ANZECC and ARMCANZ (2000) was published (Table 34).

Lowest observable effects occurred at concentrations of 3  $\mu\text{g/L}$  hexazinone in symbionts of the coral *S. hystrix*, within host tissue (Jones and Kerswell 2003) and an EC50 of 8.8  $\mu\text{g/L}$ .

Table 34: Biological effects concentrations from direct toxicity testing of hexazinone

| Species   | Effects conc.<br>µg/L | Endpoint         | Toxicity<br>measure | Reference               |
|---|-----------------------|------------------|---------------------|-------------------------|
| <b><i>Coral</i></b><br><b><i>Adult colonies</i></b> |                       |                  |                     |                         |
| <i>S. hystrix</i>                                   | 3.0                   | ↓ photosynthesis | LOEC                | Jones and Kerswell 2003 |
| <i>S. hystrix</i>                                   | 8.8                   | ↓ photosynthesis | EC50                | Jones and Kerswell 2003 |

Including these data with those in section 6.4.5 does result in sufficient data to meet the minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups, so the BurrliOZ statistical distribution method to derive a guideline trigger value can be applied. However, attempts to run the data set failed with the error message of a floating value returned. Further, as we have discussed, reduced photosynthesis endpoints are not used in derivation of guidelines.

If we apply the same interpretation as in section 6.4 that there are at least three acute EC50 or LC50 values in the data set provided, the lowest of the acute values is divided by 100 (OECD 1992) to provide a low reliability guideline trigger value. The photosynthetic endpoint becomes the lowest of the acute values and a trigger value of 0.09 µg/L results for hexazinone, which is two orders of magnitude lower than the low reliability guideline adopted in the derivation process in the section 6.4. Alternatively, in recognition of the endpoint being sublethal the divisor might be lowered to 10 and a trigger value of 0.9 µg/L results for hexazinone which is quite close to the 1.2 µg/L derived.

At this stage, with implementation of numerous management actions underway, the Great Barrier Reef Marine Park Authority sets the trigger value without the sublethal response included ie 1.2 µg/L for hexazinone. We note that this value falls below the observed LOEC of the photosynthetic effect and this gives us some confidence that it may be an effective trigger value. We recommend that additional consideration be made of the potential sublethal ecosystem effects of suppressed photosynthesis.

#### 6.6.6 2,4-D

Additional data on 2,4-D toxicity to corals has become available since ANZECC and ARMCANZ (2000) was published (Table 35).

Significant reductions in gross primary production rate, gross primary production to respiration ratio and effective quantum yield of the hermatypic coral *P. cylindrica* occurred at 100 000 µg/L concentration 2, 4-D for a period of 48 hours (Råberg et al 2003).

Using <sup>14</sup>C uptake studies, lowest observable effects on photosynthesis occurred at concentrations of 1000 µg/L 2,4-D in isolated zooxanthellae of the coral *D. strigosa*, *M. mirabilis* and *F. fragum* (Owen et al 2003).

Table 35: Biological effects concentrations from direct toxicity testing of 2,4-D

| Species                     | Effects conc.<br>µg/L | Endpoint   | Toxicity measure | Reference          |
|-----------------------------|-----------------------|--|------------------|--------------------|
| <b>Adult coral colonies</b> |                       |  |                  |                    |
| <i>P. cylindrica</i>        | 100 000               | GPP* rate, GPP to respiration ratio, effective quantum yield | LOEC             | Råberg et al, 2003 |
| <i>D. strigosa</i>          | 1000                  | ↓ <sup>14</sup> C incorporation                              | LOEC             | Owen et al 2003    |
| <i>M. mirabilis</i>         | 1000                  | ↓ <sup>14</sup> C incorporation                              | LOEC             | Owen et al 2003    |
| <i>F. fragum</i>            | 1000                  | ↓ <sup>14</sup> C incorporation                              | LOEC             | Owen et al 2003    |

\*Gross primary production

There is no acute LOEC to chronic NOEC assessment factor for 2,4-D so the assessment factor of 2.5 was applied to convert the acute LOECs to chronic NOECs in this case.

Including these responses in the BurrliOZ statistical distribution software (Campbell et al 2000) run, with the data in section 6.4.6, resulted in moderate reliability guideline trigger values of 46.5, 112 and 191 µg/L for 2,4-D for protection of 99, 95 and 90 per cent of species respectively.

At this stage, with implementation of numerous management actions underway, the Great Barrier Reef Marine Park Authority sets the trigger value without these responses included ie 0.8 µg/L and 30.8 µg/L for protection of 99 and 95 per cent of species respectively.

Additional consideration of the potential sub-lethal ecosystem effects is recommended.

### 6.6.7 Tebuthiuron

Additional data on tebuthiuron toxicity to corals has become available since ANZECC and ARMCANZ (2000) was published (Table 36).

Lowest observable effects occurred at concentrations of 10 µg/L tebuthiuron in symbionts of the coral *S. hystrix*, within host tissue (Jones and Kerswell 2003) and an EC50 of 175 µg/L.

Table 36: Biological effects concentrations from direct toxicity testing of tebuthiuron

| Species                     | Effects conc.<br>µg/L | Endpoint         | Toxicity measure | Reference               |
|-----------------------------|-----------------------|------------------|------------------|-------------------------|
| <b>Coral Adult colonies</b> |                       |                  |                  |                         |
| <i>S. hystrix</i>           | 10                    | ↓ photosynthesis | LOEC             | Jones and Kerswell 2003 |
| <i>S. hystrix</i>           | 175                   | ↓ photosynthesis | EC50             | Jones and Kerswell 2003 |

Even combining with the data presented at section 6.4.7 the minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups is not met, so the BurrliOZ statistical distribution method (Campbell et al 2000) cannot be used.

As the data set includes only one species an acute to chronic assessment factor of 1000 would normally be applied (Warne 2001). However, in recognition of the toxicity measure being based on a sublethal endpoint response, and its reversibility, an assessment factor of 100 was applied to convert the acute EC50 effects concentration to a chronic NOEC. This calculation is provided out of interest in its comparison to the freshwater guideline value and its potential consideration as a low reliability trigger value. This calculation results in a value of 1.8 µg/L for tebuthiuron,

which is between the 99<sup>th</sup> and 95<sup>th</sup> percentile freshwater guideline (0.2µg/L and 2µg/L respectively). This result increases our confidence that the adoption of the freshwater guideline trigger value aligning with the ANZECC and ARMCANZ (2000) guideline is appropriate for protecting ecosystem health.

Additional consideration of the potential sub-lethal ecosystem effects of suppressed photosynthesis is recommended.

#### 6.6.8 Chlorpyrifos / Oxon

Additional data on chlorpyrifos toxicity to microflora (Bengston Nash et al 2005a) has become available since the ANZECC and ARMCANZ (2000) guidelines were released (Table 37).

Marine diatoms sensitivities to chlorpyrifos varied widely with the most sensitive reactions (IC10) occurring at concentrations of 38 µg/L for *N. closterium* within less than 20 minutes exposure (Bengston Nash et al 2005a). *D. tertiolecta* and *P. tricornutum* showed reactions at 41 µg/L and 130 µg/L (IC10) respectively.

Table 37: Biological effects concentrations from direct toxicity testing of chlorpyrifos

| Species               | Effect conc.<br>µg/L | Endpoint         | Toxicity<br>measure | Reference                 |
|-----------------------|----------------------|------------------|---------------------|---------------------------|
| <b>Diatoms</b>        |                      |                  |                     |                           |
| <i>N. closterium</i>  | 38                   | ↓ photosynthesis | IC10                | Bengston Nash et al 2005a |
| <i>D. tertiolecta</i> | 41                   | ↓ photosynthesis | IC10                | Bengston Nash et al 2005a |
| <i>P. tricornutum</i> | 130                  | ↓ photosynthesis | IC10                | Bengston Nash et al 2005a |

The guideline trigger value has not been recalculated including this data as there is ample data without its inclusion, only IC10 are reported and an appropriate conversion factor is not known.

#### 6.6.9 Range of effect including sublethal data

Three of the pesticides had lower trigger values derived if sublethal data was included in the derivations (Table 38). Simazine and tebuthiuron actually showed higher values but still within the 99th and 95th percentile derived guidelines. The Great Barrier Reef Marine Park Authority will continue to monitor pesticide concentrations under its Marine Monitoring Program and will be keeping an eye on whether these lower figures are exceeded. If future research results support the inclusion of sublethal effects ambient concentrations may be maintained at concentrations below these in Table 38.

Table 38: Trigger value range with and without sublethal data

| Pesticide  | Range, µg/L |
|------------|-------------|
| Diuron     | 0.01-0.9    |
| Ametryn    | 0.2-0.5     |
| Hexazinone | 0.09-1.2    |

## **7 Future Research Needs**

Compilation of the available scientific literature on water quality related impacts on Marine Park ecosystems has resulted in the development of this current document. In doing so, it has become apparent that there are a number of significant knowledge gaps. The following discussion provides guidance for consideration in future research direction. Some of this guidance is extracted from the De'ath and Fabricius (2008) report to the Great Barrier Reef Marine Park Authority.

### **7.1 Sublethal effects**

There are some concerns about the adequacy of the guideline trigger values for protection of the tropical marine ecosystem. As discussed in the previous section, photosynthesis, gross primary production and carbon uptake suppression responses are not universally accepted as appropriate endpoints for deriving toxicity guidelines and have not been included in derivations of guideline trigger values. However, this response may be an indicator of sublethal impacts the minimisation of which could prove critical to the protection of the ecosystem. The concern about sublethal effects is heightened particularly if additional environmental stressors are involved, eg high temperatures, storm damage, sedimentation, grazing etc. Discussion has been included in these guidelines (section 6.6) for consideration for particular pesticides.

Species such as the coral *P. damicornis* that are dependent on photosynthesis for energy contributions are more sensitive to the effects of pesticides in terms of reproductive development and may be bioindicators of ecosystem impacts. Further research on these responses is recommended.

### **7.2 Paucity of data**

In order to ensure the health of the marine ecosystem significant consideration must be given to the preservation of food webs, in particular the primary producers. There is a paucity of data relating to the toxicity of many contaminants to those primary producers in the tropical marine ecosystem. Given the mode of action of many of the pesticides it is possible that a higher weighting should be given to effect responses that occur in plants rather than in animals. At present, no weighting is applied in the statistical distribution application and so the data will be biased tending towards the more acute mortality endpoints on animals such as fish and crustaceans that are generally less susceptible and require extrapolation to chronic effects.

A program to gather ecotoxicological response data for marine tropical primary producer organisms is recommended.

### **7.3 Toxicity of mixtures**

Additive, synergistic and antagonistic effects complicate the setting of guideline trigger values, and these are still poorly understood. For example, crustose coralline algae are far more sensitive to damage by sedimentation when traces of the herbicide diuron are present (Harrington et al 2005). Banks et al (2005) found that the toxicity effects of diazinon are significantly increased in the presence of even quite low concentrations of atrazine (although this was in freshwater). An estuarine study looking at atrazine found it to be more toxic to a particular copepod at lower salinities (Hall et al 1994), although in the same study the opposite was the case for the fish species tested (ie more toxic at higher salinity). Temperature and light were also found to

significantly influence the growth of the alga *Nannochloris oculata* and *P. tricornutum* (Mayasich et al 1986).

Other examples are that the uptake of dissolved inorganic nutrients in some benthic macro algae might be diffusion limited ie depending on both concentration and water turbulence (Hurd 2000), and that benthic macro algae can only use additional nutrients where light is not limiting.

Where mixtures are encountered the methodology for addressing this is set out in the current ANZECC and ARMCANZ guidelines.

Further research on additive, synergistic and antagonistic effects is recommended.

#### **7.4 Biogeochemistry**

Natural events generate inputs of nutrient to the marine ecosystem as well as land sourced runoff. It is important to understand these events as exceedances of guideline trigger values might result from natural events rather than from land-sources that may require management actions. For example, the primary production of the water column and the benthic compartment can increase by as much as factors of 4 and 2.5 respectively as a result of mass spawning events (Glud et al 2008). Further research effort is required on biogeochemical cycling in the marine ecosystems to improve this understanding and hence the appropriate interpretation of exceedances.

Whilst the potential ecosystem impacts of sediment have been identified, further research on the impacts of sediment associated with the organic content, biotic activity and grain size is needed for these interactive effects to become part of the guidelines. For example, high rates of sedimentation of inorganic material may not stress corals, whereas low rates of sedimentation of organically rich material stress and kill corals after 48 hours. Currently there is insufficient information available to quantitatively determine the role that elevated levels of organic carbon plays in the process of ecosystem decline in the nearshore marine environment, although enough is known to be concerned.

#### **7.5 Sedimentation**

More field data on ecosystem responses in relation to sediment quality and quantity are needed to test the sedimentation trigger value. Hydrodynamic settings determine to what extent ecosystem stress is due to sedimentation and to what extent due to turbidity. In areas of low hydrodynamic energy stress due to sedimentation will exceed the stress due to light attenuation. At high hydrodynamic energy where sediments tend to remain in suspension, the reverse is true.

In the longer term, sediment quality guidelines should be developed for the Great Barrier Reef. Such guidelines should include trigger values for sediment nutrient concentrations, which are responsible for toxicity through the development of pore water ammonia and hydrogen sulfide.

#### **7.6 Relationship between light, suspended solids and turbidity**

The relationship between light, suspended solids and turbidity (water clarity, measured either with nephelometers or as Secchi depth) depends on the nature of the particulate matter (Te 1998), and this relationship is not yet fully understood for the Great Barrier Reef. Secchi depth was used here as proxy for light, due to the good spatial coverage of the data, and because direct light measurements (eg from CTD casts) have not yet been compiled and processed for the Great Barrier Reef.

Light is a key resource for marine ecosystems, as corals and many other key groups are phototrophic organisms, and light controls coral growth (Anthony et al 2004). However, before



adequate light targets can be set, further work is needed to analyse the spatial distribution of light, its relationship to Secchi depth and turbidity, and its role in shaping the ecosystems on the Great Barrier Reef, and to better characterise hydrodynamic settings that determine whether ecosystem changes are predominantly due to sedimentation or due to turbidity.

Cooper et al (2008) have suggested long-term turbidity of greater than three NTU leads to sublethal stress, and long-term turbidity of greater than five NTU shows severe stress effects on corals at shallow depths.

## **7.7     *Hydrodynamic and biological models***

A number of coupled hydrodynamic and biological models have been developed with limited applicability (King et al 2001, Wolanski and De'ath 2005, Legrand et al 2006, Wooldridge et al 2006, Maughan et al 2007). Modelling capability that covers the whole Marine Park and its associated ecosystems is critical to understanding the linkage between river discharge and contaminant dispersal in the Great Barrier Reef lagoon.

Capacity to model the spatial and seasonal changes of lagoonal water quality will be essential to understanding residency times of contaminants, an important factor in their effect. Models indicate great variability in the residency times of water in the lagoon but agree that the lower end of the range close to the coast is generally greater than one month (Luick et al 2007, Wang et al 2007). This timeframe is well within timeframes for primary bio-available nutrients turnover (hours to two weeks), phytoplankton population generation time average (one day), pelagic development timeframe for fish, echinoderm and corals (weeks to months). Therefore contaminants that reach the marine water body remain there for biologically relevant times and are hence capable of impacting on ecosystem health.

Coupling nitrate runoff–seawater mixing zone relationships (Wooldridge et al 2006) with existing hydrodynamic modelling for the Great Barrier Reef (King et al 2001, 2002)) allows quantification of dissolved inorganic nitrogen reductions needed in the end-of-river concentrations to meet the chlorophyll *a* guideline trigger value discussed above. Currently this relationship is available for a number of river systems, from the Burdekin River to the north, that drain the catchment. Through the ongoing development of Water Quality Improvement Plans this approach is being explored for the remainder of the Great Barrier Reef.

Improved understanding of hydrodynamics sediment dispersion in the marine environment is a critical factor in facilitating management decisions to improve water quality in the Marine Park. The influences of bathymetry, wind, tidal recirculation around headlands and narrow passages, resuspension and upwellings all need to be taken into consideration.

A fine resolution grid of estimated environmental conditions should be developed for each natural resource management region based on measurements and hydrodynamic models. Such data will improve models on plume dilution, dispersal, deposition and resuspension, on biological and chemical transformations and help identifying areas of greatest risk (e.g. exposure to highest loads, highest concentrations or greatest retention).

Additional data and models are needed to identify the main factors responsible for inter- and intra-annual variability in concentrations of nutrients and suspended solids, such as the effects of river floods, wind- and wave-driven resuspension, and blooms of the nitrogen-fixing *Trichodesmium*. These factors are not well understood but should be incorporated into future models.

There are some models that deal with time varying exposure of contaminants at the community level. The comprehensive aquatic systems model (CASIM) has been used to address this challenge in theoretical ecology (DeAngelis et al 1989) and assess potential risks of chemical contaminants

to aquatic ecosystems (Bartel et al 2000, Bartel et al 1999, Naito et al 2002). CASM is a complex aquatic ecosystem model that considers water chemistry characteristics, spatial and temporal scales, and food web structure. It has not yet been used for corals but should be considered for adaptation for this purpose.

### **7.8      *Catchment action relationships***

Continued research on relationships between land use actions in individual catchments contribution to water quality conditions and ecosystem health in the estuaries, coastal seagrasses and the coral reefs of the Great Barrier Reef is essential to improved understanding and management.

The Queensland Department of Primary Industries and Fisheries are leading a Producer Demonstration Farms Project to quantify the economic and water quality benefits of particular improved management practices. Partial results from 2008 are very encouraging and highlighted some areas of the farming system where improvements such as testing and accounting for nutrients in irrigation water and use of shielded sprayers can lead to improved water quality outcomes.

Effective on farm capture and reuse of irrigation tail water has demonstrated that minimal loss of nutrients and pesticides off farm can be achieved. Strip trials testing a new slow release fertiliser show initial runoff measurements that are very promising releasing significantly less nitrate concentrations.

The Department of Natural Resources and Water and the Reef Catchments Mackay Whitsunday Group have also run a plot and paddock-scale trial on a series of practices and assessed the quality of runoff from different practices (Masters et al 2008) . Each system was treated with two different nitrogenous fertilisers and methods of residual herbicide application.

Results showed that controlled traffic farming had significantly less runoff rates than the cultivation practice on the farm under the conditions trialled. Timing of applications of herbicide to maximise the period before rainfall was most critical to minimising loss. Loss concentrations from broadcast application of herbicides were more than double those for banded applications.

Information gathered will be used to refine and improve modelling exercises through the comparison of predicted versus observed data.

### **7.9      *Reference condition***

The region of Cape York plays an important role in the Great Barrier Reef, being the only remaining coastal and midshelf reference site. The biodiversity, ecological functions and water quality conditions of the Cape York region should be much better documented and researched, before climate change and other intensifying pressures start degrading this ecosystem. Two rare category 4 - 5 cyclones and some bleaching have already disturbed some of Cape York's reefs in this region in the past five years, so it is important to obtain data from this remote region to consolidate continued use of this region as reference location. Also, Cape York should be added to any monitoring program to monitor the natural variability of reference conditions.

### **7.10    *Risk based guideline packages***

Ideally, risk based guideline packages should be developed for each ecosystem issue and ecosystem type represented in the Great Barrier Reef. These guideline packages consist of two components, a set of low risk trigger values (for key stressors) and a protocol for further investigating the risk where the trigger value is exceeded (ANZECC and ARMCANZ 2000).

Quantification of the relationships between the key stressors and environmental factors in Great Barrier Reef ecosystems has not been undertaken to date, hence no risk-based guideline packages have been developed. To facilitate the development of these guideline packages, clarification of these relationships should occur.

## 8 Conclusion

This document provides trigger values for a range of contaminants based on their effects on marine aquatic ecosystems. It is presented as a benchmark document. It is the intention that this document will be updated periodically to include new information and enhance the Great Barrier Reef Marine Park Authority's ability to manage the Marine Park for current and future generations.

The aim in any application of the guidelines is to improve the long-term protection and maintenance of the Great Barrier Reef World Heritage Area. Trigger values derived in these guidelines are presented in the following tables. Through other programs comprehensive data are being collected on current condition of waterways. Where the assessment of current condition is better than the long-term guideline trigger values presented here, or the state or national guidelines, the precautionary long-term approach is to adopt an objective that is equal to current condition so that water quality does not degrade (eg in some cases in the Mackay Whitsunday Water Quality Improvement Plan (Drewry et al 2008), Rohde et al 2008). The Great Barrier Reef Marine Park Authority wholeheartedly support the implementation of more stringent objectives.

Parameters that are not listed here default to the Queensland Water Quality Guidelines 2006, which in turn default to the Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000 (currently under review).

| Parameter                     | Water body                                      |              |          |          |
|-------------------------------|---|--------------|----------|----------|
|                               | Enclosed coastal<br>(Wet Tropics/Central Coast) | Open coastal | Midshelf | Offshore |
| Chlorophyll a (µg/L)          | 2.0   | 0.45         | 0.45     | 0.4      |
| Secchi depth <sup>1</sup> (m) | 1.0/1.5   | 10           | 10       | 17       |
| SS (mg/L)                     | 5.0/15  | 2.0          | 2.0      | 0.7      |
| PN (µg/L)                     | na  | 20           | 20       | 17       |
| PP (µg/L)                     | na  | 2.8          | 2.8      | 1.9      |

<sup>1</sup> Guideline trigger values for water clarity need to be decreased by 20 per cent for areas with greater than 5 m tidal ranges eg Broad Sound.

na Guideline trigger values are not currently available for these parameters for enclosed coastal waters.

For the following parameters, the trigger values are chosen to be applied in the Great Barrier Reef Marine Park case regardless of the current condition of the ecosystems, or indeed regardless of the flow of water. Therefore, only single values are set and apply equally to the water bodies.

| Parameter          | Guideline trigger value  |
|--------------------|--|
| Sedimentation rate | Maximum mean annual sedimentation rate of 3 mg/cm <sup>2</sup> /d, and a daily maximum of 15 mg/cm <sup>2</sup> /d |
| Sea temperature    | Increases of no more than 1°C above the long-term average maximum  |

High, moderate and low reliability guideline trigger values were derived for listed pesticides, and for tributyltin, where sufficient marine specific data were available. Where there was insufficient data the trigger values from the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000* are repeated here. All pesticide and biocide trigger values are set protective of 99 per cent of species.

| <b>Pesticide</b> | <b>Trigger value, µg/L</b>  |
|------------------|-----------------------------|
|                  | <b>High reliability</b>     |
| Chlorpyrifos     | 0.0005                      |
|                  | <b>Moderate reliability</b> |
| Diuron           | 0.9                         |
| Atrazine         | 0.6                         |
| Ametryn          | 0.5                         |
| 2,4-D            | 0.8                         |
| Endosulfan       | 0.005                       |
|                  | <b>Low reliability</b>      |
| Simazine         | 0.2                         |
| Hexazinone       | 1.2                         |
| Tebuthiuron      | 0.02                        |
| MEMC             | 0.002                       |
| Diazinon         | 0.00003                     |
| <b>Biocide</b>   | <b>High reliability</b>     |
| Tributyltin      | <b>0.0004*</b>              |

\* In recognition of their slightly to moderately disturbed systems state existing approved spoil dumping ground guideline trigger values are set protective of 95 per cent of species. Refer to section 6.5.

The trigger values identified in these guidelines are not targets, but are guideline trigger values that, when exceeded, trigger management responses. Management responses are a part of the adaptive management strategies in Water Quality Improvement Plans in the Great Barrier Reef catchments and in regional natural resource management plans.

We know that under present conditions concentrations sometimes exceed those set in these guidelines (particularly in flood events). Many actions are already being undertaken to improve water quality and as those are widely implemented in the catchments the situation is expected to improve. Careful consideration will be made of any monitoring results that are over the trigger values in deciding if any action is needed. The Great Barrier Reef Marine Park Authority acknowledge and emphasise the importance of working with people to set appropriate short-term and long-term targets for the catchments that they live in, and supporting activities in their area that will improve local water quality and subsequently protect the health of the Great Barrier Reef.

These guidelines define trigger values that will be used to:

- Support setting targets for water quality leaving catchments
- Prompt management actions where trigger levels are exceeded
- Encourage strategies to minimise release of contaminants
- Identify further research into impacts of contaminants in the Marine Park
- Assess cumulative impacts on the Great Barrier Reef ecosystems at local and regional levels
- Provide an information source for natural resource management bodies, industry, government and communities.

The guidelines will be revised from time to time as we find out more about our systems and their responses to different conditions. Comments on the guidelines are invited at any time and can be made to:

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PO Box 1379  
Townsville QLD 4810  
Or by email to:

wqguide@gbmpa.gov.au

## Appendices

### Appendix 1: Pesticides

#### 1.1 Diuron

Diuron is a long acting (residual) herbicide that has been registered in Australia for more than 20 years. Diuron kills weeds by inhibiting the process of photosynthesis, this means that plants cannot convert sunlight energy to grow. It is absorbed by the plant via the root system.

The half life of diuron varies from 5 days to 372 days depending on soil type and aerobic/anaerobic conditions.

In Australia there are currently 88 registered products containing diuron. Diuron is used to kill weeds both before and after emergence. Most of the uses are in agriculture to control all types of weeds in sugarcane, cotton, broadacre crops (oats, wheat, barley), citrus and some horticultural crops such as pineapples and bananas. It is also used to control weeds in irrigation channels and drainage ditches. Diuron is used as a component of antifouling paints, to protect boats from marine growth, in home aquariums and ponds to prevent algal growth and for weed control around buildings, railway lines, sheds and driveways.

Key findings of the 2005 Australian Pesticides and Veterinary Medicines Authority review into the use of diuron included that:

- there is a risk to the environment caused by diuron in water and soil runoff from use in sugarcane, cotton, citrus, horticultural crops and in irrigation channels and drainage ditches; and
- the risk to the environment can be reduced by decreasing the environmental load (through reducing application of diuron).

Australian Pesticides and Veterinary Medicines Authority (2005) *Diuron review – FAQ*.  
[http://www.apvma.gov.au/chemrev/diuron\\_FAQ.shtml](http://www.apvma.gov.au/chemrev/diuron_FAQ.shtml) (Accessed 14 September 2006)

#### 1.2 Atrazine

Atrazine is a selective, systemic herbicide that provides knockdown and residual action for control of many broad-leaved weeds and some grasses in tree plantations and a variety of crops such as sorghum, maize, canola and sugarcane. Atrazine is one of the most widely used herbicides in Australian agriculture. The chemical does not adsorb strongly to soil particles and has a lengthy half-life (60 to >100 days). Atrazine has a high potential for groundwater contamination despite its moderate solubility in water. Sunlight and saline conditions speed-up atrazine degradation rates (Brambilla et al 1993) resulting in a half-life less than 30 days in estuarine systems (Huber 1993). Tropical soil conditions also shorten atrazine's half life.

A 1997 National Registration Authority for Agricultural and Veterinary Chemicals (NRA) review found that atrazine continues to demonstrate the potential to contaminate ground and surface water and that safety margins for aquatic organisms are, in some circumstances, narrow. The NRA recommended that measures be taken to reduce aquatic contamination, and that levels of atrazine and its major metabolites in the environment be monitored to determine trends in atrazine contamination of surface and ground waters and to establish whether current and future restrictions are effective in maintaining or improving safety margins.

National Registration Authority for Agricultural and Veterinary Chemicals. Review of Atrazine (1997)  
<http://www.apvma.gov.au/chemrev/atsum.shtml> - [Toc392061205](http://www.apvma.gov.au/chemrev/atsum.shtml#Toc392061205) (Accessed 14 September 2006)  
IPEN Body Burden Community Monitoring Handbook: Chemical Fact Sheet (2002)  
[http://www.oztoxics.org/cmwg/chemicals/rbapts\\_chem/Atrazine.html](http://www.oztoxics.org/cmwg/chemicals/rbapts_chem/Atrazine.html) (Accessed 14 September 2006)

#### 1.3 Ametryn

Ametryn, a member of the Triazine chemical family, is a herbicide which inhibits photosynthesis and other enzymatic processes. It is used to control broadleaf weeds and annual grasses in pineapple, sugarcane and bananas.

Ametryn's half-life in soils, the amount of time it takes to degrade to half of the original concentration, is 70 to 250 days, depending on the soil type and weather conditions. Loss from the soil is principally by microbial degradation (1, 3). Ametryn moves both vertically and laterally in soil due to its high water solubility (5). Because it is persistent, it may leach as a result of high rainfall, floods, and furrow irrigation (1).

Ametryn is moderately toxic to fish. The LC50 for rainbow trout exposed for 96 hours is 8.8 mg/l. The LC50 for bluegill is 4.1 mg/l and for goldfish it is 14.1 mg/l (2, 3). Ametryn is highly toxic to crustaceans and moderately to highly toxic to mollusks (4).

Cornell University. The Extension Toxicology Network.

<http://pmep.cce.cornell.edu/profiles/extoxnet/24d-captan/ametryn-ext.html> (Accessed 26 September 2006).

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3. The Agrochemicals Handbook, Third Edition. 1994. Royal Society of Chemistry Information Systems, Unwin Brothers Ltd., Surrey, England.
4. Briggs, Shirley. 1992. Basic Guide to Pesticides. Hemisphere Publishing. Washington, DC.
5. Thomson, W. T. 1982. Agricultural Chemicals Book II Herbicides. Thomson Publications. Fresno, CA.

### 1.4 Simazine

Simazine (2-chloro-4,6-bis(ethylamino)-s-triazine) is a synthetic chemical that is widely used as an herbicide to control the growth of weeds. Its primary agricultural use is to control broad-leaf and grassy weeds in corn fields, citrus crops, alfalfa and grapes. It is also used to control weeds in strawberries, apples, pears, nuts, olives, pineapples, asparagus, sugar cane, tea and coffee. It is often used as a *pre-emergent herbicide* to control weeds before the new seedlings emerge from the soil. Its non-agricultural uses have included weed control on vacant lots and right-of-ways.

It is a photosynthesis inhibitor. Its half-life is 30 days (Hamilton and Haydon 1997 cited in McMahon et al 2003). It has a soil adsorption coefficient of 100 (McMahon et al 2003).

There is some evidence that simazine persists in soil. About half of the simazine is still present in soil 12 days to two years after its application. Over time, some of the simazine is broken down by bacteria in the soil. More information is needed on the persistency of these simazine breakdown products in soil, and their potential to leach into ground and surface water.

Cornell University. The Sprecher Institute for Comparative Cancer Research. Division of Cancer and Environment.

<http://envirocancer.cornell.edu/FactSheet/Pesticide/fs16.simazine.cfm> (Accessed 26 September 2006).

### 1.5 Hexazinone

Hexazinone is a contact and residual herbicide. It is a photosynthetic inhibitor, effective for reducing competition from broad leaf trees and bushes, as well as annual and perennial weeds.

In natural stream water hexazinone half-life has been reported to be greater than 56 days by Kollman and Segawa (1995) and Linders et al (1994), and more than 260 days by Bouchard et al (1985). Soil hexazinone studies have determined half-lives of 10 to 275 days (Neary et al 1983, Bouchard et al 1985, Michael 1990, Kollman and Segawa 1995). Linders et al (1994) classified hexazinone as "slightly degradable" with a half-life of 62 days.

Hexazinone is mobile in the environment and partitions into water more than to soil, or biota. In Linders et al (1994) hexazinone is classified as moderately mobile in soil. Bouchard and Lavy (1985) found that hexazinone is weakly adsorbed by soil, in fact, less adsorbed by soil and more mobile than atrazine. Also, hexazinone is the most water-soluble triazine herbicide. With the moderate to long half-life and moderate mobility, hexazinone can potentially move off-site with water in runoff and in baseflow.

Department of Pesticide Regulation, Sacramento, USA. Environmental Monitoring & Pest Management Branch. **Environmental fate of hexazinone.** Ganapathy, C.



<http://www.cdpr.ca.gov/docs/empmpubs/fatememo/hxzineone.pdf> - search=%22hexazinone%22

(Accessed 26 September 2006).

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Michael, J.L. 1990. Fate of Hexazinone After Application for Pine Planting Site Preparation. E.I. du Pont de Nemours and Co., Inc. Wilmington, DE. Document No. AMR 1786-90. unpublished study. DPR #396-062.

Neary, D. G., P. B. Bush, and J. E. Douglass. 1983. Off-site movement of hexazinone in stormflow and baseflow from forest watersheds. *Weed Sci.* 31:543-551.

### 1.6 2,4-D

2,4-D is an herbicide in the phenoxy or phenoxyacetic acid family that is used as a post emergent broadleaf weed control. It causes disruption of plant hormone responses including disruption of multiple growth processes in susceptible plants by affecting proteins in the plasma membrane, interfering with RNA production, and changing the properties and integrity of the plasma membrane. The plant's vascular system becomes blocked and inhibits the vascular transport system.

2,4-D acid is non-persistent in terrestrial environments (half life = 6.2 days), moderately persistent in aerobic aquatic environments (half life = 45 days), and highly persistent in anaerobic terrestrial and aquatic environments (half life = 231 days). Because 2,4-D acid will be anionic under most environmental conditions, it is expected to be highly mobile in soil and aquatic environments.

Marine invertebrate LC50 s ranged from >0.092 to >66 mg ae/l for the 2,4-D butoxyethyl ester (BEE).

US EPA. Environmental Fate and Effects Division's Risk Assessmentfor the Reregistration Eligibility Document for 2,4-Dichlorophenoxyacetic Acid (2,4-D). Corbin,  
<http://www.epa.gov/espp/effects/24d/attachment-b.pdf> (Accessed 26 September 2006).

### 1.7 Tebuthiuron

Tebuthiuron is a broad-spectrum herbicide used to control weeds in non-cropland areas, rangelands, rights-of-way, and industrial sites. It is effective on woody and herbaceous plants in grasslands and sugar cane. It is a photosynthesis inhibitor.

Tebuthiuron is highly persistent in soil with reported half-lives from 12 to 15 months in areas with over 40 inches annual rainfall, with longer half-lives expected in drier areas or in soils with high organic matter content [1]. Tebuthiuron is broken down slowly in the soil through microbial degradation. Breakdown by sunlight is negligible, as is volatilisation (or evaporation from the soil surface) [1]. It is poorly bound to soil, suggesting high mobility. In field studies, however, little or no lateral movement has been seen in soils with appreciable clay or organic matter content [1].

EXTOXNET. Extension Toxicology Network. Pesticide Information Profile.

Cooperative Extension Offices of Cornell University, Oregon State University, the University of Idaho, and the University of California at Davis and the Institute for Environmental Toxicology, Michigan State Uni.  
<http://extoxnet.orst.edu/pips/tebuthiu.htm> (Accessed 27 September 2006).

REFERENCES: 1. Weed Science Society of America. Herbicide Handbook, Seventh Edition. Champaign, IL, 1994.9-5

### 1.8 Chlorpyrifos / chloropyrifos oxon

Chlorpyrifos is a broad-spectrum organophosphate insecticide. It is registered for use in Australia for crop protection and pest control. In agricultural applications, chlorpyrifos is registered to control a broad range of insect pests across many crops. In domestic and commercial settings it is registered for the control of pests such as termites, fleas and cockroaches. It is also registered for use in cat and dog flea shampoos and collars, and in flea sprays for dogs (Queensland health).

It acts by inhibiting an enzyme involved in neural transmissions (Humphrey and Klumpp 2003).

It has a relatively persistent nature, with a half-life between 29 and 74 days in water (Racke 1993 cited in Humphrey and Klumpp 2004). It is not persistent in the water column so spot sampling can miss it. Continuous samplers are recording its occurrence in marine water bodies of the Great Barrier Reef (Muller, pers. comm.). Its detection is of concern, particularly for the early life stages of corals and fish.

Chlorpyrifos is one of the most widely used insecticides in Queensland sugar industry being applied at rates of up to 74 tonne per year across Queensland (Hamilton and Haydon 1996).

### 1.9 Endosulfan

Endosulfan is a broad spectrum organochlorine insecticide for the control of a large variety of insects and mites in crops.

It is moderately persistent in the soil environment with a reported average field half-life of 50 days. The two isomers have different degradation times in soil (half-lives of 35 and 150 days for  $\alpha$ - and  $\beta$ -isomers, respectively, in neutral conditions). It has a moderate capacity to adsorb to soils and it is not likely to leach to groundwater. In plants, endosulfan is rapidly broken down to the corresponding sulfate, on most fruits and vegetables, 50 per cent of the parent residue is lost within three to seven days.

Endosulfan is highly to moderately toxic to bird species (Mallards: oral LD50 31 - 243 mg/kg) and it is very toxic to aquatic organisms (96-hour LC50 rainbow trout 1.5  $\mu\text{g/L}$ ). It has also shown high toxicity in rats (oral LD50: 18 - 160 mg/kg, and dermal: 78 - 359 mg/kg). There is a strong evidence of its potential for endocrine disruption.

Concentrations of endosulfan in sediments from Queensland sugar and cane farms have been found up to 840  $\mu\text{g/kg}$  (Muller et al 2000).

IPEN Body Burden Community Monitoring Handbook: Chemical Fact Sheet (2002)  
[http://www.oztoxics.org/cmwg/chemicals/rbapts\\_chem/Endosulfan.html](http://www.oztoxics.org/cmwg/chemicals/rbapts_chem/Endosulfan.html) (Accessed 27 September 2006).

### 1.10 MEMC

2-Methylethyl mercuric chloride (MEMC) is a fungicide.

More than 500 kg of the fungicide methylethylmercuric chloride was applied each year for 40 years in one Great Barrier Reef catchment (Johnson & Ebert 2000 cited in Markey et al, in press). Great Barrier Reef sediment cores have identified mercury concentrations of up to 100  $\mu\text{g kg}^{-1}$ , an order of magnitude higher than background concentrations (Walker and Brunskill 1997 cited in Markey et al 2007). These concentrations were attributed to the contemporary application of mercury-based fungicides on sugar cane farms (Markey et al 2007).

### 1.11 Diazinon

Diazinon is an organophosphate insecticide used to control insects that acts by inhibiting neuromuscular system activity (Pesando et al 2003).

Its persistence in the environment is generally considered reasonably short (1-2 months). Pesando et al (2003) however cites Dauberschmidt et al (1996) as reporting that it may persist in sediments for longer, and cites Romero et al (1989) that effects in organisms may last several months due to persistence in the blood.

It has a low persistence in soil. The half-life is two to four weeks [1]. Bacterial enzymes can speed the breakdown of diazinon and have been used in treating emergency situations such as spills [2]. Diazinon seldom migrates below the top half inch in soil, but in some instances it may contaminate groundwater.

Breakdown rate in water is dependent on the acidity. At highly acidic levels, one half of the compound disappeared within 12 hours while in a neutral solution, the pesticide took six months to degrade to one half of the original concentration [2].

In plants, a low temperature and a high oil content tend to increase the persistence [3]. Generally the half-life is rapid in leafy vegetables, forage crops and grass. The range is from two to 14 days.

EXTOXNET. Extension Toxicology Network. Pesticide Information Profile.

Cooperative Extension Offices of Cornell University, Oregon State University, the University of Idaho, and the University of California at Davis and the Institute for Environmental Toxicology, Michigan State Uni. <http://extoxnet.orst.edu/pips/diazinon.htm> (Accessed 27 September 2006).

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## **Appendix 2: Other contaminants**

### **2.1 Tributyltin**

Organotin compounds are potent toxins, and this property has led to their use in a range of biocides including ship antifouling paints. Their use on large ships is extensive, with most of the world's ocean-going fleet reliant on their use to inhibit fouling growth (Michel and Avery 1999). Tributyltin (TBT) based antifoulant paints have been used in Australia since the early 1970s, although use on vessels smaller than 25m was banned in Eastern Australian States in 1989 in response to growing evidence of environmental impacts in semi-enclosed waters subject to intensive shipping or ship-related activity (Wilson et al 1993, Batley 1996, Evans 1999). Butyltins are highly toxic to a range of marine reef biota including scleractinian corals (Morse et al 1988, Allemand et al 1998, Negri and Heyward 2001), octocorals (Sebens 1983), other cnidarians (Mercier et al 1996, Leitz 1997) and molluscs (Labare et al 1997), and bryozoans (Kitamura and Hirayama 1987). Its mode of action is primarily through disruption of the functioning of cell membranes (Viarengo 1989, Fent 1996), and microcosm experiments have demonstrated its effectiveness against organisms that recruit to hard substrata (Henderson 1988).

### **2.2 Dioxins**

Dioxins are a group of 210 chlorinated compounds consisting of chlorinated dibenzopara-dioxins (PCDDs) and chlorinated dibenzofurans (PCDFs). They are formed during various chemical and industrial manufacturing processes and by combustion of organic material (Kjeller et al 1991), and also via lesser-known natural processes (Hashimoto et al 1995, Alcock et al 1998). Dioxins are known to display a diverse and complex array of toxicological properties (Buckland et al 1990) and have been detected in a variety of environmental compartments including freshwater and marine sediments (Czuzwa and Hites 1984, Rappe et al 1987, Jonsson et al 1993, Mosse and Haynes 1993) and the tissue of marine mammals (Buckland et al 1990, Muir et al 1996, Haynes et al 1999).

A summary of the findings of studies on the effects of dioxins conducted from 2001-2004 was published in 2004 (Department of the Environment and Heritage (2004)).

### **2.3 Organochlorines**

Chlorinated organic compounds (or organochlorines) are carbon-based chemicals that contain bound chlorine. These compounds are mostly artificial and enter the environment mainly through human activities. However, it is now recognised that marine algae and invertebrates and natural processes such as forest fires also contribute variable quantities of organochlorines to the environment (Leach et al. 1985; Enell and Wennberg 1991; Gribble 1994). Chlorinated organic compounds have had a wide range of industrial and agricultural applications, although many of them are now banned from use. They include pesticides such as DDT (dichloro-diphenyl-trichloroethane) and lindane ( $\gamma$ -HCH or gamma-hexachlorocyclohexane) and polychlorinated biphenyls (PCBs).

The few studies of the impacts of organochlorine compounds carried out in Australian freshwater and marine environments indicate that environmental contamination by organochlorine substances has occurred at relatively low concentrations in Australia. Highest concentrations have been associated with centres of urbanisation (Richardson 1995). This contamination pattern is similar to the findings of studies elsewhere which have identified chlorinated organic compounds in estuarine and marine sediments near major metropolitan areas along the eastern coast of the United States and at a wide range of locations in Europe and Asia associated with human settlement (Alvarez Piñeiro et al 1995; Mohapatra et al 1995; Thompson et al. 1996; Agnihotri et al 1996).

Organochlorine pesticides enter the environment via a number of routes following their release or application. They enter the atmosphere directly during spraying, and later following volatilisation of deposited spray from both foliage and surface soil (Nash and Hill 1990). They also enter the atmosphere adsorbed to wind-blown dust particles (Clark 1992), which are ultimately re-deposited on land or water. Applied and deposited pesticides are transported from application and depositional sites to the aquatic environment in overland flows and ground leachate following rainfalls (Clendening et al. 1990). Organochlorine compounds can also enter the environment as contaminants contained in effluent discharges and in urban stormwater runoff. Organochlorine compounds are highly hydrophobic and once in the water column, tend to adsorb to fine particulates or be bioaccumulated into lipids in aquatic biota (Olsen et al 1982). The final distribution of organochlorine compounds between the different phases in the aquatic environment is complex (Connell 1995). The consequences of organochlorine tissue accumulation

are also complex (Clark 1992) and organochlorine pesticides and polychlorinated biphenyls (PCBs) have been implicated in reproductive and immunological abnormalities observed in terrestrial bird populations and in marine mammal populations (Boon et al. 1992). While the impact of organochlorines are still unclear for lower invertebrates such as corals, and their potential toxicity to immune systems and reproductive processes is of concern.

The persistent nature of many of these and related contaminants, together with possible continued illegal use of banned chloro-hydrocarbon compounds raises the potential for continued long-term chronic exposure to plants and animals of the Great Barrier Reef.

## **2.4 Heavy Metals**

Heavy metals are natural constituents of rocks and soils and enter the environment as a consequence of weathering and erosion. Many metals are biologically essential, but all have the potential to be toxic to biota above certain threshold concentrations. Following industrialisation, unnatural quantities of metals such as arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), nickel (Ni) and zinc (Zn) have been released, and continue to be released into the aquatic environment through agricultural, urban stormwater and wastewater discharges. As, Cd, Cu, Hg and Zn are the metals with the most potential impact that enter the environment as a consequence of agricultural activity. Zn and Cu are used in small amounts as fertilisers in some soils deficient in these elements, and As, Cd and Hg are constituents of some fungicides (Hunter 1992). Cu is also used as an algaecide and Cd and Zn occur as contaminants of phosphatic fertilisers (Rayment et al. 1989). Another metallic compound, organotin, has no natural counterparts and is generally introduced into the marine environment through biocide applications, principally as constituents of antifouling paints (Witney unpublished report).

Metals are strongly associated with particulates and enter the marine environment in a similar fashion to organochlorine compounds. They mostly enter the environment via the atmospheric transport of dust and through sediment movement in overland flows and in waterways (Bryan 1971). Additional quantities of metals are also added to the environment via the discharge of effluent and urban stormwater. Particulate metals in suspension and in bottom sediments are not generally directly available to aquatic organisms. The exception to this is sediment bound metals, which can be accumulated following solubilisation in the acidic juices of a sediment-feeder's gut (Waldichuk 1985). The rates at which metals are solubilised from particulates is dependent on environmental factors including dissolved oxygen concentrations, pH, salinity and temperature (Waldichuk 1985). Once dissolved in the water column, metals may be accumulated by marine invertebrates from solution via passive uptake across permeable surfaces such as gills and the digestive tract (Rainbow 1990). Cellular metal toxicity is primarily due to the chemical inactivation of cellular enzymes responsible for normal organism survival and function (1989). Organism growth, reproduction and behaviour are also potentially affected by elevated environmental metal concentrations (Langston 1990).

## List of Abbreviations and Acronyms

|              |   |
|--------------|---|
| ac .....     | active constituent  |
| ae .....     | acid equivalent   |
| AIMS .....   | Australian Institute of Marine Science  |
| ANZECC ..... | Australian and New Zealand Environment and Conservation Council   |
| APVMA.....   | Australian Pesticides and Veterinary Medicines Authority  |
| ARMCANZ..... | Agricultural and Resource Management Council of Australia and New Zealand   |
| CASM.....    | Comprehensive aquatic systems model   |
| CCI .....    | Coastal Catchments Initiative   |
| chl .....    | chlorophyll   |
| CL.....      | confidence level  |
| cm .....     | centimetre  |
| d.....       | day   |
| DEWHA .....  | Department of the Environment, Water, Heritage and the Arts (previously Department of the Environment and Heritage)                                   |
| EC10.....    | The concentration of a test substance resulting in an effect on 10% of the test species   |
| EC50.....    | The concentration of a test substance resulting in an effect on 50% of the test species   |
| EPA .....    | Environmental Protection Agency   |
| GBRMPA ..... | Great Barrier Reef Marine Park Authority  |
| h.....       | hour  |
| IC50 .....   | The concentration of a test substance resulting in an inhibition of a given biological process (or component of a process) in 50% of the test species |
| L.....       | litre   |
| LC50.....    | Concentration (for example, in water, food or soil) resulting in a 50% mortality of the test organism.  |
| LOEC.....    | Lowest Observed Effect Concentration ie the test concentration at which some effect occurs  |
| MEMC.....    | 2-methylethyl mercuric chloride   |
| mg.....      | milligram   |
| NOEC .....   | No Observed Effect Concentration ie the test concentration at which no effect is observed   |
| NRA.....     | National Registration Authority (precursor agency to the APVMA)   |
| NTU .....    | Nephelometric Turbidity Unit  |
| NWQMS.....   | National Water Quality Management Strategy  |
| OECD .....   | Organisation for Economic Co-operation and Development  |
| PN.....      | particulate nitrogen  |
| PP.....      | particulate phosphorus  |
| RED .....    | Re-registration Eligibility Document  |
| SS.....      | suspended solids  |
| SSD.....     | Species Sensitivity Distribution  |
| µg.....      | micrograms  |

## Glossary

|                                  |  |
|----------------------------------|--|
| Active constituent               | Active constituents are the substance/s in an agvet chemical product primarily responsible for a product's biological or other effects   |
| Acute                            | Rapid adverse effect caused by a substance in a living organism. Can define either the exposure or the response to an exposure. This document applies acute exposure for multi-celled organisms as being less than or equal to 96 hours, and for single-celled organisms as being less than 72 hours (Warne 2001)  |
| Ambient waters                   | Surrounding waters, generally of largely natural occurrence  |
| Assessment factor                | A unitless number applied to the lowest toxicity effect figure for a chemical to derive a concentration that should not cause adverse environmental effects in the absence of sufficient data to apply more rigorous derivation methods  |
| Aquatic ecosystem                | Any watery environment, from small to large, from pond to ocean, in which plants and animals interact with the chemical and physical features of the environment   |
| Benthic                          | Referring to organisms living in, or on, the sediments of aquatic habitats   |
| Biomass                          | The living weight of a plant or animal population, usually expressed on a unit area basis  |
| Catchment                        | The total area draining into a river, reservoir, or other body of water including the Great Barrier Reef lagoon  |
| Chronic                          | Lingering or continuing adverse effect caused by a substance in a living organism for a long time; often for periods of several weeks to years. Can define either the exposure or the response to and exposure (effect). This document applies chronic exposure for multi-celled organisms as being greater than 96 hours, and for single-celled organisms as being equal to or greater than 72 hours (Warne 2001) |
| Concentration                    | The quantifiable amount of chemical in, say, water, food or sediment   |
| Contaminant                      | Biological (eg bacterial and viral pathogens) and chemical (see Toxicant) introductions capable of producing an adverse response (effect) in a biological system, seriously injuring structure or function or resulting in death   |
| Criteria                         | Scientific data  |
| Desorption                       | Removal of an absorbed material from a surface   |
| Direct toxicity assessment/ test | The use of toxicity tests to determine the acute and/or chronic toxicity of a particular contaminant on an organism  |
| Ecosystem health                 | The ability of an ecosystem to support and maintain key ecological processes and organisms so that their species compositions, diversity and functional organisations are as comparable as possible to those occurring in natural habitats within a region   |
| Enclosed coastal water body      | The water body adopted from the Queensland Water Quality Guidelines 2006. Refer to text at section 3.2 for full description  |
| Endpoint                         | Measured attainment response   |
| Environmental values             | Particular values or uses of the environment that are important for a healthy ecosystem or for public benefit, welfare, safety or health and that require protection from the effects of pollution, waste discharges and deposits. Several environmental values may be designated for a specific waterbody   |
| Fertilization                    | The fusion of gametes to produce a new organism of the same species  |
| Geometric mean                   | A type of mean or average, which indicates the central tendency or typical value of a set of numbers. It is similar to the arithmetic mean, which is what most people think of with the word "average," except that instead of adding the set of numbers and then dividing the sum by the count of numbers in the set, $n$ , the numbers are multiplied and then the $n$ th root of the resulting product is taken |

|  |   |
|--|---|
| Guideline                                    | Numerical concentration limit or narrative statement recommended to support and maintain a particular water use. In the Great Barrier Reef Marine Park the use is the function of aquatic ecosystems  |
| High reliability guideline trigger value     | Trigger values that have a higher degree of confidence because they are derived from chronic no observed effect concentration (NOEC) toxicity data for five different species that belong to at least four different taxonomic groups (Warne 2001)  |
| Inhibition                                   | A restraining of the function of a particular process or sequence   |
| Inshore                                      | In most cases, the water body commencing at the seaward edge of the open coastal water body (0.1 across the continental shelf) and continuing to the relative distance of 0.4 across the continental shelf assuming the shoreline has a value of zero, and the edge of the continental shelf has a value of one. In general text referenced to other authors the inshore water body may also include open coastal and enclosed coastal water body |
| Low reliability guideline trigger value      | Trigger values that have a low degree of confidence because they are derived from an inadequate data set. They are derived using either assessment factors or from modelled data or by adopting freshwater guideline trigger values.  |
| Median                                       | Middle value in a sequence of numbers   |
| Metamorphosis                                | A biological process by which an animal physically develops after birth or hatching, involving a conspicuous and relatively abrupt change in the animal's form or structure through cell growth and differentiation   |
| Midshelf water body                          | The water body commencing at the seaward edge of the open coastal water body and continuing to the relative distance of 0.4 across the continental shelf assuming the shoreline has a value of zero, and the edge of the continental shelf has a value of one. Referred to in De'ath and Fabricius (2008) as the inshore water body   |
| Moderate reliability guideline trigger value | Trigger values that have a moderate degree of confidence because they are derived from a minimum data requirement (Warne 2001) of five different species that belong to at least four different taxonomic groups, and applying into the BurliOZ statistical distribution method (Campbell et al 2000)   |
| Mortality                                    | The condition of susceptibility to death  |
| Offshore water body                          | The water body commencing at the seaward edge of the midshelf water body and continuing to the relative distance of one across the continental shelf assuming the shoreline has a value of zero, and the edge of the continental shelf has a value of one   |
| Open coastal water body                      | The water body commencing at the seaward edge of the enclosed coastal water body and continuing to the relative distance of 0.1 across the continental shelf assuming the shoreline has a value of zero, and the edge of the continental shelf has a value of one. Referred to in De'ath and Fabricius (2008) as the coastal water body   |
| Parameter                                    | A measurable or quantifiable characteristic or feature  |
| Percentile                                   | Division of a frequency distribution into one hundredths  |
| Pesticide                                    | A substance or mixture of substances used to kill unwanted species of plants or animals   |
| Photosynthesis                               | The conversion of carbon dioxide to carbohydrates in the presence of chlorophyll using light energy   |
| Physico-chemical                             | Refers to the physical (eg temperature, electrical conductivity) and chemical (eg concentration of nitrate, mercury) characteristics of water   |
| Primary production                           | The production of organic matter from inorganic materials   |
| Reference condition                          | An environmental quality or condition that is defined from as many similar systems as possible and used as a benchmark for determining the environmental quality or condition to be achieved and/or maintained in a particular system of equivalent type  |



|                   |  |
|-------------------|--|
| SedNet            | A web-based management tool that constructs sediment budgets for river networks to identify patterns in the material fluxes. This can assist effective targeting of catchment and river management actions to improve water quality and riverine habitat   |
| Sorption          | Process whereby contaminants in soil adhere to the inorganic and organic soil particles  |
| Species richness  | The number of species present (generally applied to a sample or community)   |
| Sublethal effects | Below the level that causes death  |
| Tolerance         | The ability of an organism to withstand adverse or other environmental conditions for an indefinitely long exposure without dying  |
| Toxicant          | A chemical capable of producing an adverse response (effect) in a biological system at concentrations that might be encountered in the environment, seriously injuring structure or function or producing death  |
| Toxicity test     | The means by which the toxicity of a chemical or other test material is determined. A toxicity test is used to measure the degree of response produced by exposure to a specific level of stimulus (or concentration of chemical)  |
| Toxicology        | The study of the nature and effects of poisons   |
| Trigger value     | Concentration (or other measure) of the particular parameter measured for the ecosystem, below which there exists a low risk that adverse biological (ecological) effects will occur. They indicate a risk of potential impact if exceeded and should 'trigger' some action, either implementation of management/remedial action, or closer investigation to identify if the value has been set at the appropriate level for the particular organism |
| Zooplankton       | The animal portion of the plankton   |
| Zooxanthellae     | Intracellular endosymbionts of various marine animals and protozoa, especially anthozoans such as the scleractinian corals and the tropical sea anemone, <i>Aiptasia</i>   |

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